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11

SPACE CHARGE IN SOLID DIELECTRICS

This chapter is devoted to the study of space charge build up and measurement of charge density within the dielectric in the condensed phase. When an electric field is applied to the dielectric polarization occurs, and so far we have treated the polarization mechanisms as uniform within the volume. However, in the presence of space charge the local internal field is both a function of time and space introducing non-linearities that influence the behavior of the dielectrics. This chapter is devoted to the recent advances in experimental techniques of measuring space charge, methods of calculation and the role of space charge in enhancing breakdown probability. A precise knowledge of the mechanism of space charge formation is invaluable in the analysis of the polarization processes and transport phenomena.

11.1 THE MEANING OF SPACE CHARGE

Space charge occurs whenever the rate of charge accumulation is different from the rate of removal. The charge accumulation may be due to generation, trapping of charges, drift or diffusion into the volume. The space charge may be due to electrons or ions depending upon the mechanism of charge transfer. Space charge arises both due to moving charges and trapped charges.

Fig. 11.1 shows the formation of space charge due to three processes in a dielectric that is subjected to an electric field¹.

(a) The electric field orients the dipoles in the case of a homogenous material and the associated space charge is a sharp step function with two peaks at the electrodes.

(b) Ion migration occurs under the influence of the electric field, with negative charges migrating to the positive electrode and vice-versa. The mobility of the various carriers

are not equal and therefore the accumulation of negative charges in the top half is random. Similarly the accumulation space charge due to positive charges in the bottom portion is also random and the voltage due to this space charge is also arbitrary. The space charge is called “heterocharges”.

(c) Charges injected at the electrodes generate a space charge when the mobility is low. The charges have the same polarity as the electrode and are called “homocharges.”

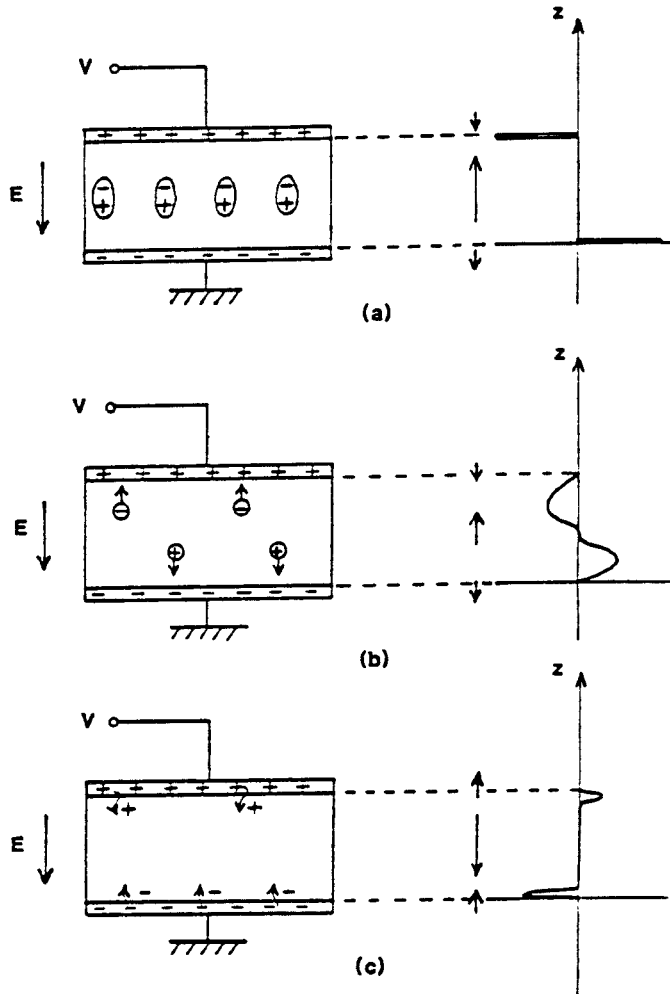


Fig. 11.1 Development of charge distribution $\rho(z)$ in a dielectric material subjected to an electric field. (a) dipole orientation, (b) ion migration, (c) charge transfer at the interfaces (Lewiner, 1986, © IEEE).

A modern treatment of space charge phenomenon has been presented by Blaise and Sarjeant² who compare the space charge densities in metal oxide conductors (MOS) and high voltage capacitors (Table 11.1). The effect of moving charges is far less in charging of the dielectric and only the trapped charges influence the internal field.

11.2 POLARONS AND TRAPS

The classical picture of a solid having trapping sites for both polarities of charge carriers is shown earlier in Fig. 1.11. The concept of a polaron is useful in understanding the change in polarization that occurs due to a moving charge.

Table 11.1

Electronic space charge densities in MOS and HV capacitors (Blaise and Sargent, 1998)
(with permission of IEEE)

Parameter	unit	MOS		HV capacitors	
		Mobile	Trapped	Mobile charges	Trapped charges
mobility	m ² /Vs	~20×10 ⁻⁴		10 ⁻⁷ -10 ⁻⁴	
Current density	A/m ²	10-10 ⁴		10 ⁻² -0.1	
Applied field	MV/m	100-1200	100-1200	10-100	10-100
Charge density	C/m ³	20μ-0.02	300-30,000	200μ-0.02	-
Charge conc.	/m ³	10 ⁻⁸ -10 ⁻⁵	0.1-0.01	2×10 ⁻⁸ -2×10 ⁻⁶	10 ⁻³ -10

An electron moving through a solid causes the nearby positive charges to shift towards it and the negative charges to shift away. This distortion of the otherwise regular array of atoms causes a region of polarization that moves with the electron. As the electron moves away, polarization vanishes in the previous location, and that region returns to normal. The polarized region acts as a negatively charged particle, called polaron, and its mass is higher than that of the isolated charge. The polarization in the region due to the charge is a function of the distance from the charge. Very close to the charge, ($r < r_e$), where r is the distance from the charge and r_e is the radius of the sphere that separates the polarized region from the unpolarized region. When $r > r_e$ electronic polarization becomes effective and when $r > r_i$, ion polarization occurs.

Let us consider a polaron of radius r_p in a dielectric medium in which a fixed charge q exists. The distance from the charge is designated as r and the dielectric constant of the medium varies radially from ϵ_∞ at $r_1 < r_p$ to ϵ_s at $r_2 > r_p$. The binding energy of the polaron is, according to Landau³

$$W = -\frac{1}{4\pi} \left[\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right] \frac{q^2}{r_p} \quad (11.1)$$

where r_p is the radius of the polaron, ϵ_∞ and ϵ_s are the dielectric constants which shows that smaller values of r_p increase the binding energy. This is interpreted as a more localized charge. The localization of the electron may therefore be viewed as a coupling between the charge and the polarization fields. This coupling causes lowering of the potential energy of the electron.

The kinetic energy determines the velocity of the electron which in turn determines the time required to cross the distance of a unit cell. If this time is greater than the characteristic relaxation time of electron in the ultraviolet region, then the polarization induced by the electron will follow the electron almost instantaneously. The oscillation frequencies of electron polarons is in the range of 10^{15} - 10^{16} Hz. If we now consider the atomic polarization which has resonance in infrared frequencies, a lower energy electron will couple with the polarization fields and a lattice polaron is formed. The infrared frequency domain is 10^{12} - 10^{13} Hz and therefore the energy of the electron for the formation of a lattice polaron is lower, on the order of lattice vibration energy. The lattice polaron has a radius, which, for example in metal oxides, is less than the interatomic distance.

Having considered the formation of polarons we devote some attention to the role of the polarons in the crystal structure. Fig. 11.2(a) shows the band structure in which the band corresponding to the polaron energy level is shown as $2J_p$ [Blaise and Sargent, 1998]. At a specific site i (11.2b) due to the lattice deformation the trap depth is increased and therefore the binding energy is increased. This is equivalent to reducing the radius of the polaron, according to equation (11.1), and therefore a more localization of the electron. This variation of local electronic polarizability is the initiation of the trapping mechanism.

Trapping centers in the condensed phase may be classified into passive and active centers. Passive centers are those associated with anion vacancies, that can be identified optically by absorption and emission lines. Active trapping centers are those associated with substituted cations. These are generally of low energy ($\sim 1\text{eV}$) and are difficult to observe optically. These traps are the focus of our attention.

11.3 A CONCEPTUAL APPROACH

Focusing our attention on solids, a simple experimental setup to study space charge is shown in fig. 11.3⁴. The dielectric has a metallic electrode at one end and is covered by a conducting layer which acts as a shield. The current is measured through the metallic end. The charges may be injected into the solid by irradiation from a beam of photons, X-rays or gamma rays. Photons in the energy range up to about 300 keV interact with a

solid, preferentially by the photoelectric effect. Photons above this energy interact by Compton effect; an increase of wavelength of electromagnetic radiation due to scattering by free or loosely bound electrons, resulting in absorption of energy (Gross, 1978). The secondary electrons are scattered mainly in the forward direction. The electrons move a certain distance within the dielectric, building up a space charge density and an internal electric field which may be quite intense to cause breakdown.

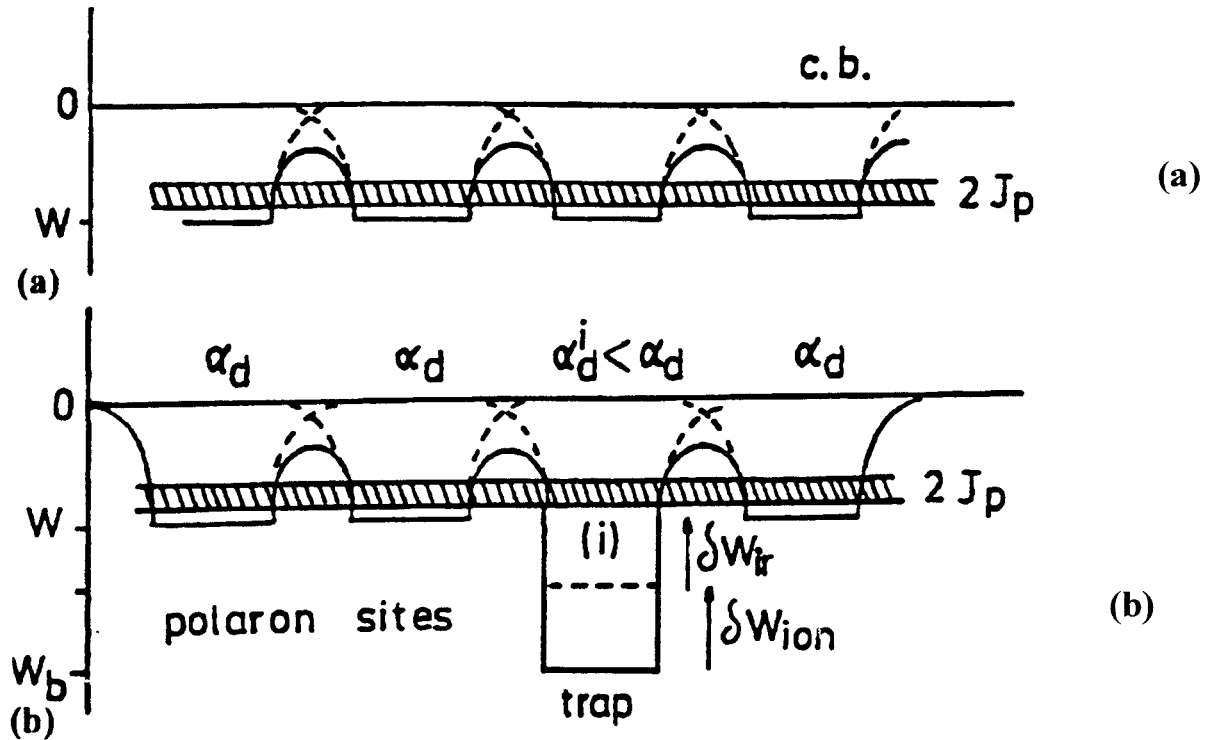


Fig. 11.2 (a) Potential wells associated with polaron sites in a medium of uniform polarizability, forming a polaron band of width $2J_p$. (b) Trapping effect due to a slight decrease of electronic polarizability on a specific site i , ($\alpha_d^i < \alpha_d$). The charge is stabilized at the site due to lattice deformation. This leads to the increase of trap depth by an amount δW_{ion} . The total binding energy is $W_b = \delta W_{ir} + \delta W_{ion}$ (Blaise and Sargent, 1998, © IEEE).

The space charge build up due to irradiation with an electron beam is accomplished by a simple technique known as the 'Faraday cup'. This method is described to expose the principle of space charge measurements. Fig. 11.4 shows the experimental arrangement used by Gross, et al⁵. A dielectric is provided with vacuum deposited electrodes and irradiated with an electron beam. The metallic coating on the dielectric should be thin enough to prevent absorption of the incident electrons. The electrode on which the irradiation falls is called the "front" electrode and the other electrode, "back electrode". Both electrodes are insulated from ground and connected to ground through separate

current measuring instruments. The measurements are carried out in either current mode or voltage mode and the method of analysis is given by Gross, et al.⁶

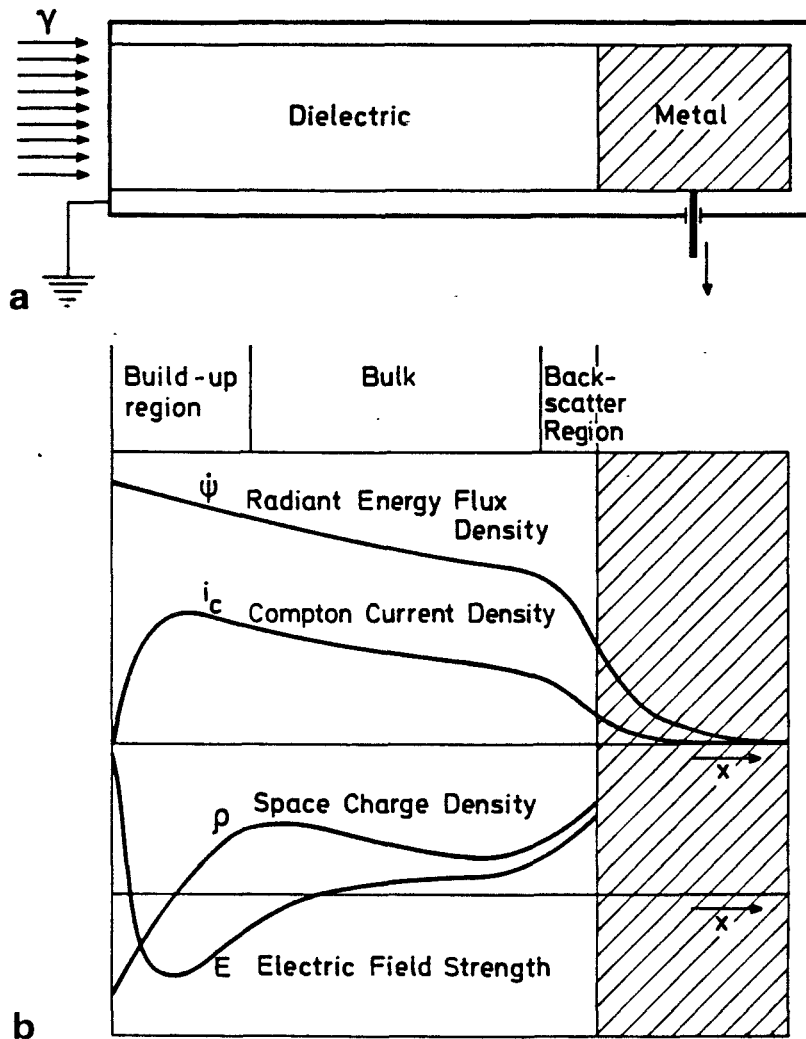


Fig. 11.3 (a) Technique for measurement of current due to charge injection. (b) Schematic for variation of space charge density and electric field strength (Gross, 1978, ©IEEE).

Electrical field, particularly at high temperatures, also augments injection of charges into the bulk creating space charge. The charge responsible for this space charge may be determined by the TSD current measurements described in the previous chapter. In amorphous and semicrystalline polymers space charge has a polarity opposite to that of the electrode polarity; positive polarity charges in the case of negative poling voltage and vice-versa. The space charge of opposite polarity is termed heterocharge whereas space charge of the same polarity is termed homocharge. In the case of the heterocharges the local space charge field will intensify the applied field, whereas in the case

of homo charges there will be a reduction of the net field. In the former case of heterocharges, polarization that occurs in crystalline regions will also be intensified.

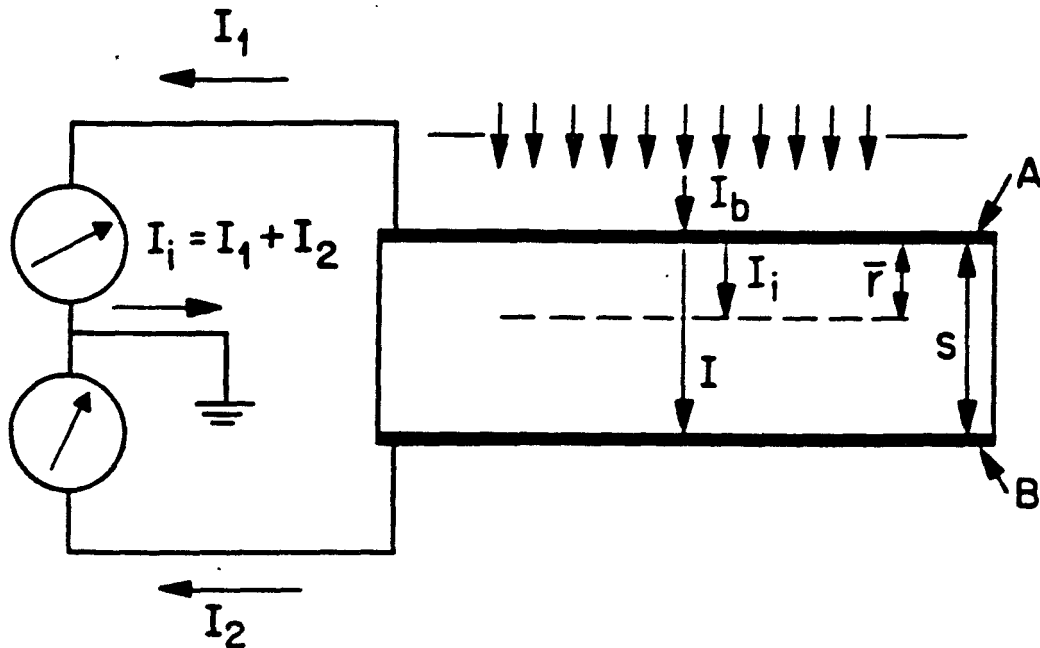


Fig. 11.4 Split Faraday cup arrangement for measurement of charge build up and decay. A- Front electrode, B-back electrode, s-thickness of dielectric, $\bar{r}$ -center of gravity of space charge layer. The currents are: I_i -injection current, I_1 -front electrode current, I_2 =rear current, I =dielectric current (Gross et. al. 1973, with permission of A. Inst. Phys.).

The increase in internal electric field leads to an increase of the dielectric constant ϵ' at high temperatures and low frequencies, as has been noted in PVDF and PVF⁷. It is important to note that the space charge build up at the electrode-dielectric interface also leads to an increase of both ϵ' and ϵ'' due to interfacial polarization as shown in section 4.4. It is quite difficult to determine the precise mechanism for the increase of dielectric constant; whether the space charge build up occurs at the electrodes or in the bulk. Obviously techniques capable of measuring the depth of the space charge layer shed light into these complexities.

The objectives of space charge measurement may be stated as follows:

- (1) To measure the charge intensities and their polarities, with a view to understanding the variation of the electric field within the dielectric due to the applied field.
- (2) To determine the depth of the charge layer and the distribution of the charge within that layer.
- (3) To determine the mechanism of polarization and its role in charge accumulation.

(4) To interpret the space charge build up in terms of the morphology and chemical structure of the polymer

In the sections that follow, the experimental techniques and the methods employed to analyze the results are dealt with. Ahmed and Srinivas⁸ have published a comprehensive review of space charge measurements, and we follow their treatment to describe the experimental techniques and a sample of results obtained using these techniques. Table 11.2 presents an overview of the methods and capabilities.

11.4 THE THERMAL PULSE METHOD OF COLLINS

The thermal pulse method was first proposed by Collins⁹ and has been applied, with improvements, by several authors. The principle of the method is that a thermal pulse is applied to one end of the electret by means of a light flash. The flash used by Collins had a duration of 8μs. The thermal pulse travels through the thickness of the polymer, diffusing along its path. The current, measured as a function of time, is analyzed to determine the charge distribution within the volume of the dielectric. The experimental arrangement is shown in Fig. 11.5.

The electret is metallized on both sides (40 nm thick) or on one side only (lower fig. 11.5), with an air gap between the electret, and a measuring electrode on the other. By this method voltage changes across the sample are capacitively coupled to the electrode. The gap between the electrode and the electret should be small to increase the coupling. The heat diffuses through the sample and changes in the voltage across the dielectric, $\Delta V(t)$, due to non-uniform thermal expansion and the local change in the permittivity, are measured as a function of time. The external voltage source required is used to obtain the zero field condition which is required for equations (11.3) and (11.4) (see below).

Immediately after the heat pulse is applied, temperature changes in the electret are confined to a region close to the heated surface. The extent of the heated zone can be made small by applying a shorter duration pulse. The process of metallizing retains heat and the proportion of the retained heat can be made small by reducing the thickness of the metallizing. In the ideal case of a short pulse and thin metallized layer, the voltage change after a heat pulse applied is given by

$$\rho_T = \int_0^d \rho(x) dx \quad (11.2)$$

where ρ_T is the total charge density (C/m^2). Determination of the total charge in the electret does not require a deconvolution process.

Table 11.2

Overview of space charge measuring techniques and comments (Ahmed and Srinivas, 1997). R is the spatial resolution and t the sample thickness.

(with permission of IEEE)

Method	Disturbance	Scan mechanism	Detection process	r (μm)	t (μm)	Comments
Thermal pulse method	Absorption of short-light pulse in front electrode	Diffusion according to heat-conduction equations	Voltage change across sample	≥ 2	~ 200	High resolution requires deconvolution
Laser intensity modulation method	Absorption of modulated light in front electrode	Frequency-dependent steady-state heat profile	Current between sample electrodes	≥ 2	~ 25	Numerical deconvolution is required
Laser induced pressure pulse method	Absorption of short laser light pulse in front electrode	Propagation with longitudinal sound velocity	Current between sample electrodes	1	100 – 1000	No deconvolution is required
Thermoelastically generated LIPP	Absorption of short laser light pulse in thin burned layer	Propagation with longitudinal sound velocity	Current or voltage between sample electrodes	1	50 – 70	Deconvolution is required
Pressure wave propagation method	Absorption of short laser light pulse in metal target	Propagation with longitudinal sound velocity	Voltage or current between sample electrode	10	5 – 200	Resolution improved with deconvolution Also used for surface charge measurements
Non-structured acoustic pulse method	HV spark between conductor and metal diaphragm	Propagation with longitudinal sound velocity	Voltage between sample electrode	1000	≤ 10000	Used for solid and liquid dielectric Higher resolution with deconvolution
Laser generated acoustic pulse method	Absorption of short laser light pulse in thin paper target	Propagation with longitudinal sound velocity	Voltage between sample electrodes	50	≤ 3000	Deconvolution is required Target and sample immersed in dielectric liquid
Acoustic probe method	Absorption of laser light pulse in front electrode	Propagation with longitudinal sound velocity	Voltage between sample electrodes	200	2000 – 6000	
Piezoelectrically-generated pressure step method	Electrical excitation of piezoelectric quartz plate	Propagation with longitudinal sound velocity	Current between sample electrodes	1	25	Deconvolution is required
Thermal step method	Applying two isothermal sources across sample	Thermal expansion of the sample	Current between sample electrodes	150	2000 – 20000	Deconvolution is required
Electro-acoustic stress pulse method	Force of modulated electric field on charges in sample	Propagation with longitudinal sound velocity	Piezoelectric transducer at sample electrode	100	≤ 10000	Deconvolution is required Also used for surface charge measurements
Photoconductivity method	Absorption of narrow light beam in sample	External movement of light beam	Current between sample electrodes	≥ 1.5	—	Nondestructive for short illumination time
Space charge mapping	Interaction of polarized light with field	parallel illumination of sample volume or movement of light beam or sample	Photographic record	200	—	Mostly used on transparent dielectric liquids
Spectroscopy	Absorption of exciting radiation in sample	External movement of radiation source or sample	Relative change in the observed spectrum	≥ 50	—	Few applications
Field probe	None	Capacitive coupling to the field	Current	1000	≤ 20000	Destructive

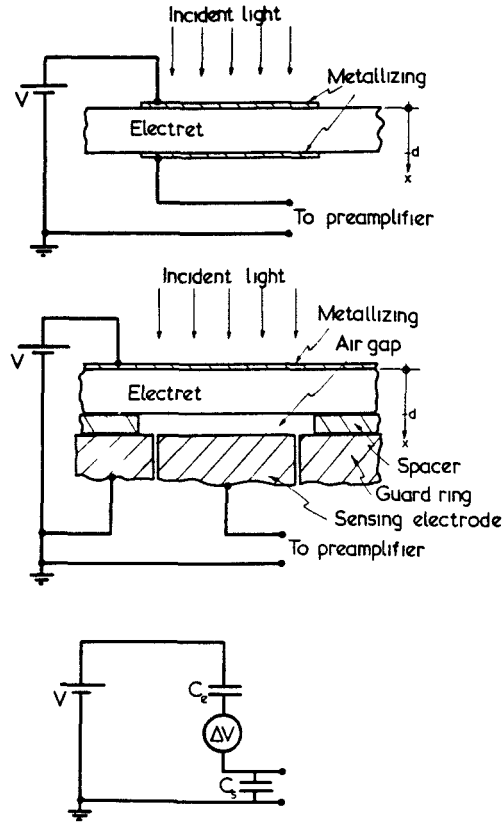


Fig. 11.5 Schematic diagram of the apparatus for the thermal pulsing experiment in the double metallizing and single metallizing configurations. (Collins, 1980, Am. Inst. Phys.)

The observed properties of the electret are in general related to the internal distribution of charge $\rho(x)$ and polarization $P(x)$ through an integral over the thickness of the sample. The potential difference V_0 across the electret under open circuit conditions (zero external field) is given by

$$V_0 = \frac{1}{\epsilon_s \epsilon_0} \int_0^d [x \rho(x) + P(x)] dx \quad (11.3)$$

where $\rho(x)$ is the charge density in C/m^3 and d the thickness of the sample.

Collins (1980) derived the expression

$$\Delta V(t) = \frac{1}{\epsilon_s \epsilon_0} \int_0^d \left\{ \left[A \rho(x) - B \frac{dP}{dx} \right] \int_0^x \Delta T(x') dx' \right\} dx \quad (11.4)$$

where $A = \alpha_x - \alpha_e$ and $B = \alpha_p - \alpha_x - \alpha_e$, x is the spatial coordinate with $x = 0$ at the pulsed electrode. $\rho(x)$ and $P(x)$ are the spatial distributions of charge and polarization. The symbols α mean the following:

- α_x = Thermal coefficient of expansion
- α_e = Temperature coefficient of the dielectric constant
- α_p = Temperature coefficient of the polarization

There are two integrals, one a function of charge and the other a function of temperature. Two special cases are of interest. For a non-polar dielectric with only induced polarization $P = 0$, equation (11.4) reduces to

$$\Delta V(t) = \frac{(\alpha_x - \alpha_e)}{\epsilon_s \epsilon_0} \int_0^d \left\{ \left[\rho(x) \right] \int_0^x \Delta T(x') dx' \right\} dx \quad (11.5)$$

For an electret with zero internal field

$$\rho(x) = + \frac{dP}{dx} \quad (11.6)$$

$$\Delta V(t) = \frac{\alpha_p}{\epsilon_s \epsilon_0} \int_0^d P(x) \Delta T(x, t) dx \quad (11.7)$$

Collins used a summation procedure to evaluate the integral in equation (11.5). The continuous charge distribution, $\rho(x)$ is replaced by a set of N discrete charge layers ρ_n with center of gravity of each layer at mid point of the layer and having coordinate $x_j = (j - \frac{1}{2})d/N$ with $j = 1, 2, \dots, N$. The integral with the upper limit x in equation (11.5) is replaced with the summation up to the corresponding layer x_j . Equation (11.5) then simplifies to

$$\Delta V(t) = \frac{(\alpha_x - \alpha_e)}{\epsilon_s \epsilon_0} \sum_{j=1}^N \rho_j \left(\sum_{i=1}^j \Delta T_i \right) \quad (11.8)$$

Assuming a discrete charge distribution the shape of the voltage pulse is calculated using equation (11.8) and compared with the measured pulse shape. The procedure is repeated till satisfactory agreement is obtained. Collins' procedure does not yield a unique distribution of charge as a deconvolution process is involved.

The technique was applied to fluoroethylenepropylene (FEP, Teflon™) electrets and the depth of charge layer obtained was found to be satisfactory. Polyvinylidene fluoride (PVDF) shows piezo/pyroelectric effects, which are dependent on the poling conditions. A copolymer of vinylidene fluoride and tetrafluoroethylene (VF₂-TFE) also has very large piezoelectric and pyroelectric coefficients. The thermal poling method has revealed the poling conditions that determine these properties of the polymers. For example, in PVDF, a sample poled at lower temperatures has a large spatial non-uniformity in the polarization across its thickness. Even at the highest poling temperature some non-uniformity exists in the spatial distribution of polarization. Significant differences are observed in the polarization distribution, even though the samples were prepared from the same sheet.

Seggern¹⁰ has examined the thermal pulse technique and discussed the accuracy of the method. It is claimed that the computer simulations show that the only accurate information available from this method is the charge distribution and the first few Fourier coefficients.

11.5 DEREGGI'S ANALYSIS

DeReggi et al.¹¹ improved the analysis of Collins (1980) by demonstrating that the voltage response could be expressed as a Fourier series. Expressions for the open circuit conditions and short circuit conditions are slightly different, and in what follows, we consider the former¹².

The initial temperature at $(x,0)$ after application of thermal pulse at $x=0$, $t=0$ may be expressed as

$$T(x,0) = T_1 + \Delta T(x,0) \quad (11.9)$$

where T_1 is the uniform temperature of the sample before the thermal pulse is applied, and $\Delta T(x,0)$ is the change due to the pulse. $\Delta T(x,0)$ is a sharp pulse extending from $x = 0$ with a width $s \ll d$. From equation (11.9) it follows that the temperature at x after the application of the pulse is

$$T(x,t) = T_1 + \Delta T(x,t) \quad (11.10)$$

where

$$\Delta T(x,t) = a_0 + \sum_{n=1}^{\infty} a_n \cos\left[\frac{n\pi x}{d}\right] \exp\left[\frac{-n^2 t}{T_1}\right] \quad (11.11)$$

$$a_0 = d^{-1} \int_0^d \Delta T(x,0) dx = \lim_{t \rightarrow \infty} \Delta T(x,t) \quad (11.12)$$

$$a_n = \frac{2}{d} \int_0^d \Delta T(x,0) \cos\left[\frac{n\pi x}{d}\right] dx; \quad n = 1, 2, \dots \quad (11.13)$$

The temperature at the surface is given by

$$\Delta T(0,t) = a_0 + \sum_{n=1}^{\infty} a_n \exp\left[\frac{-n^2 t}{\tau}\right] \quad (11.14)$$

$$\Delta T(x,t) = a_0 + \sum_{n=1}^{\infty} (-1)^n a_n \exp\left[\frac{-n^2 t}{\tau}\right] \quad (11.15)$$

where $\tau = d^2/\pi^2 K$ and k is called thermal diffusivity. The dimensionless quantities $\Delta T(0,t)/a_0$ and $\Delta T(d, t)/a_0$ can be obtained by measuring the transient resistance of one or both the electrodes. Then the ratios a_n/a_0 and τ_1 can be determined without knowing the detailed shape of the light pulse.

Substituting equation (11.15) into (11.5) the voltage at time t is given as

$$\Delta V(t) = \frac{\alpha_x - \alpha_\varepsilon}{\varepsilon_s \varepsilon_o} \left[\alpha_o A_o + \frac{d}{n} \sum_{n=1}^{\infty} \frac{a_n A_n}{n} \exp\left(\frac{-n^2 t}{T_1}\right) \right] \quad (11.16)$$

where the following relationships hold.

$$A_o = \int_0^d x \rho(x) dx \quad (11.17)$$

$$A_n = \int_0^d \rho(x) \sin\left(\frac{n\pi x}{d}\right) dx \quad (11.18)$$

The terms a_n and A_n are the coefficients of Fourier series expansions for $\Delta T(x,0)$ and $\rho(x)$ respectively, if these are expanded as cosine and sine terms, respectively.

For the short circuit conditions, equations for the charge distribution and the polarization distribution are given by Mopsik and DeReggi (1982, 1984). About 10-15 coefficients could be obtained for real samples, based on the width of the light pulse. The polarization distribution determined will be unique as a deconvolution procedure is not resorted to. Fig. 11.6 shows the results for a nearly uniformly poled polyvinylidene fluoride (PVF₂) which was pulsed alternately on both sides. An interesting observation in this study is that there is a small peak just before the polarization falls off.

A further improvement of the thermal pulse technique is due to Suzuoki et. al.¹³ who treat the heat flow in a slab in the same way as electrical current in an R-C circuit with distributed capacitance. The electrical resistance, capacitance, current and voltage are replaced by the thermal resistance R_i , thermal capacitance C_i , heat flow $q(x, t)$ and temperature $T(x, t)$, respectively.

The basic equations are:

$$-\frac{\partial q(x,t)}{\partial x} = C_i \frac{\partial T(x,t)}{\partial t} \quad (11.19)$$

$$-\frac{\partial T(x,t)}{\partial x} = R_i \frac{\partial q(x,t)}{\partial t} \quad (11.20)$$

The heat flux is given by

$$\frac{q(x,t)}{q_0} = 1 - \frac{x}{l} - \frac{2}{\pi} \sum_{k=1}^{\infty} \frac{1}{k} \exp\left(-\frac{k^2 \pi^2 t}{\tau}\right) \left(\frac{k \pi x}{l}\right) \quad (11.21)$$

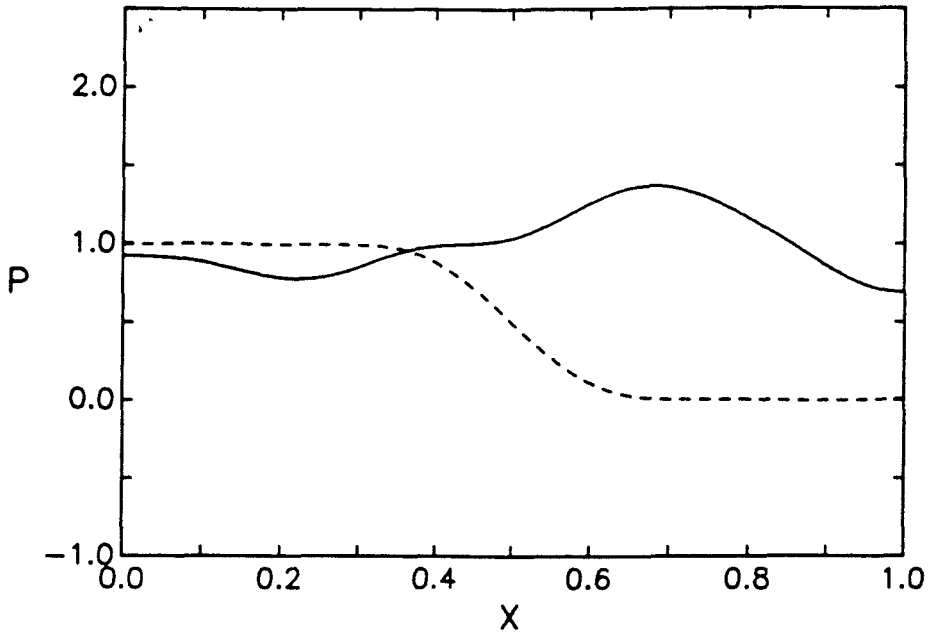


Fig.11.6 Polarization in PVF₂ sample. The solid line is experimental distribution. The dashed line is the resolution expected for a step function, at $x = 0.5$ (DeReggi, et al., 1982, with permission of J. Appl. Phys.).

The total current in the external circuit at $t = 0$, when the specimen is illuminated at $x = 0$ is given by

$$j_1(0) = -\frac{\alpha q_0}{C_l l^2} \int_0^d (d-x) \rho(x) dx \quad (11.22)$$

Similarly, the current, when the specimen is illuminated at $x = d$, is

$$j_2(0) = -\frac{\alpha q_0}{C_l l^2} \int_0^d x \rho(x) dx \quad (11.23)$$

The total amount of space charge is

$$Q_l = -\frac{C_l l}{\alpha q_0} [j_1(0) + j_2(0)] \quad (11.24)$$

The mean position of the space charge is

$$\frac{\bar{x}}{l} = \frac{j_2(0)}{j_1(0) + j_2(0)} \quad (11.25)$$

The thermal pulse was applied using a xenon lamp and the pulse had a rise time of 100 μ s, width 500 μ s. Since the calculated thermal time constant was about 5ms, the light pulse is an approximation for a rectangular pulse. The materials investigated were HDPE and HDPE doped with an antistatic agent. Fig. 11.7 shows the measured currents in doped HDPE. Homocharges were identified at the anode and in doped HDPE a strong heterocharge, not seen in undoped HDPE, was formed near the cathode.

11.6 LASER INTENSITY MODULATION METHOD (LIMM)

Lang and Das Gupta¹⁴ have developed this method which is robust in terms of data accuracy and requires only conventional equipment, as opposed to a high speed transient recorder, which is essential for the thermal pulse method. A thin polymer film coated with evaporated opaque electrodes at both surfaces is freely suspended in an evacuated chamber containing a window through which radiant energy is admitted. Each surface of the sample, in turn, is exposed to a periodically modulated radiant energy source such as a laser. The absorbed energy produces temperature waves which are attenuated and retarded in phase as they propagate through the thickness of the specimen. Because of the attenuation, the dipoles or space charges are subjected to a non uniform thermal force to generate a pyro-electric current which is a unique function of the modulation frequency and the polarization distribution.

Let $\omega \text{ rad s}^{-1}$ be the frequency of the sinusoidally modulated laser beam and the specimen illuminated at $x = d$. The surface at $x = 0$ is thermally insulated. The heat flux absorbed by the electrode is $q(d, t)$ which is a function of the temperature gradient along the thickness. The one dimensional heat flow equations are solved to obtain the current as

$$I(\omega) = \frac{C\omega(j+1)}{D \sinh D(j+1)d} \int_0^d P(x) \cosh D(j+1)x dx \quad (11.26)$$

where $D = (\omega/2K)^{1/2}$, j is the complex number operator and C contains all the position and frequency-dependent parameters. The current generated lags the heat flux because of the phase retardation of the thermal wave as it progresses through the film. The current therefore has a component in phase and in quadrature to the heat flux.

The mathematical treatment of measured currents at a number of frequencies for determining $P(x)$ involves the following steps: The integral sign in equation (11.26) may be replaced by a summation by dividing the film into n incremental thickness, each layer having its polarization, P_j , where $j=1,2,\dots,n$. The matrix equation $[I] = [G] [P]$ where

$$\begin{aligned} [I] &= I(\omega_k); \\ [G] &= \frac{[C\omega(i+1)\cosh D(i+1)x]}{[D\sinh D(i+1)d]} \\ [P] &= P_k \end{aligned} \quad (11.27)$$

is solved. The in-phase component of measured current is used with the real part of G and the quadrature component is used with the imaginary part. It is advantageous to measure $I(\omega)$ at more than n frequencies and apply the least square method to solve for P .

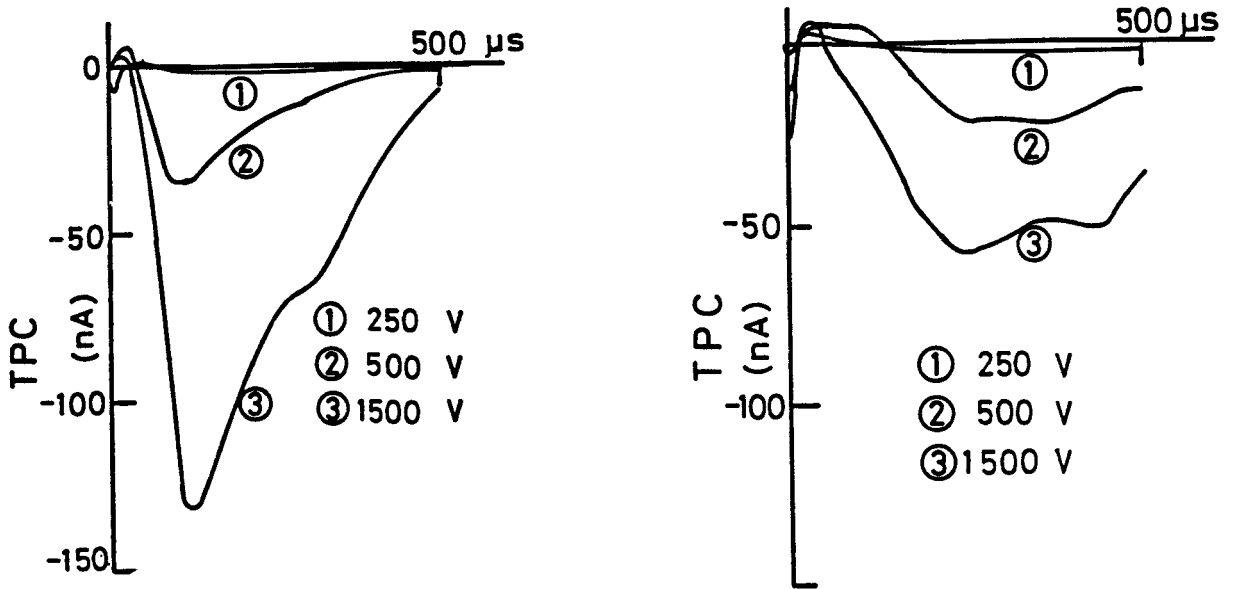


Fig. 11.7 Experimental thermal pulse currents in doped HDPE for (a) cathode illumination (b) anode illumination. Negative currents show the existence of a positive space charge in the sample (Suzuoki et al, 1985; with permission of Jap. J. Appl. Phys.)

Fig. 11.8 shows the polarization distributions and pyroelectric currents versus frequency. Because of the impossibility of producing an experimentally precise type of polarization, a triangular distribution was assumed and the currents were synthesized. Using the in-phase and quadrature components of these currents, the polarization distribution was calculated as shown by points. The parameters used for these calculations are $d = 25.4 \mu\text{m}$, $K = 0.1 \times 10^{-7} \text{ m}^2\text{s}^{-1}$, $10^2 < f < 10^5 \text{ Hz}$ (101 values), obtaining 51 values of P_k . Lang

and Das Gupta (1981) have used the LMM technique to study spatial distribution of polarization in PVDF and thermally poled polyethylene.

11. 7 THE PRESSURE PULSE METHOD

The principle of the pressure pulse method was originally proposed by Laurenceau, et al.¹⁵ and will be described first. There have been several improvements in techniques that will be dealt with later. The pressure probe within a dielectric causes a measurable electrical signal, due to the fact that the capacitance of a layer is altered in the presence of a stress wave. The pressure pulse contributes in two ways towards the increase of capacitance of a dielectric layer. First, the layer is thinner than the unperturbed thickness due to the mechanical displacement carried by the wave. Second, the dielectric constant of the compressed layer is increased due to electrostriction caused by the pulse¹⁶.

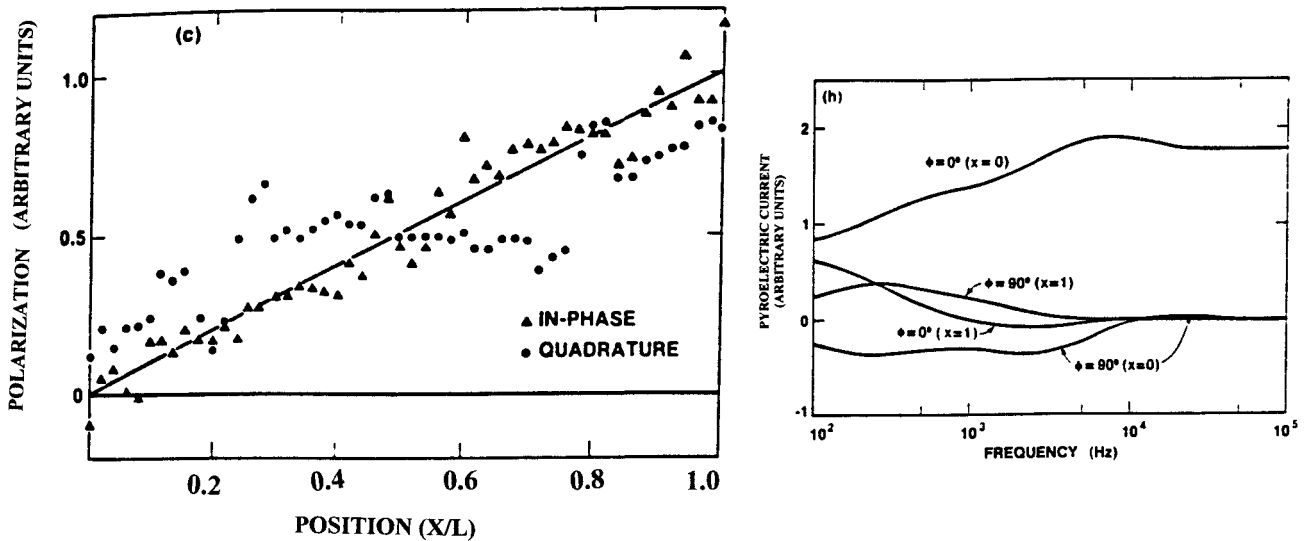


Fig. 11.8 (a) Pyroelectric current versus frequency ($x = 0$ and $x = d$ refers to heating from $x = 0$ and $x = d$ side of the film. $\phi = 0$ and $\phi = \pi/2$ refers to in phase or in quadrature with heat flux respectively. (b) Polarization distributions (solid line) and calculated distributions (points). Selected data from (Lang and Das Gupta, 1981, with permission of Ferroelectrics).

A dielectric slab of thickness d , area A , and infinite-frequency dielectric constant ϵ_∞ with electrodes a and b in contact with the sample, is considered. The sample has acquired, due to charging, a charge density $\rho(x)$ and the potential distribution within the dielectric is $V(x)$. All variables are considered to be constant at constant x ; the electrode a is grounded, electrode b is at potential V . The charge densities σ_a and σ_b are given by

$$\sigma_a = -\frac{d - \langle x \rangle}{d} \frac{Q}{A} - \varepsilon_\infty \frac{V}{d} \quad (11.28)$$

$$\sigma_b = \frac{\langle x \rangle}{d} \frac{Q}{A} + \varepsilon \frac{V}{d} \quad (11.29)$$

where

$$\langle x \rangle = \frac{\int_0^d x \rho(x) dx}{\int_0^d \rho(x) dx} \quad \text{and} \quad \frac{Q}{A} = \int_0^d \rho(x) dx \quad (11.30)$$

Expressions (11.28) and (11.29) show that if $V = 0$ and if the sample is not piezoelectric, a uniform deformation along the x axis does not alter the charges on the electrodes since $(d - \langle x \rangle)/d$ remains constant. This implies that in order to obtain the potential or charge profiles, a non-homogeneous deformation must be used. A step function compressional wave propagating through the sample with a velocity v , from electrode **a** towards **b**, provides such a deformation. As long as the wave front has not reached the opposite electrode, the right side of the sample is compressed while the left part remains unaffected (Fig. 11.9). The charge induced on electrode **b** is a function of the charge profile, of the position of the wave front in the sample, but also of the boundary conditions at the electrodes: Open circuit or short circuit conditions. In the first case the observable parameter is the voltage, in the second case, the external current.

Let the unperturbed thickness of the sample be d_0 , and Δp the magnitude of pressure excess in the compressed region, β the compressibility of the dielectric defined as the fractional change in volume per unit excess pressure, $\beta = -\Delta V/(V\Delta p)$. The compressed part of the dielectric has a permittivity of ε' and x_f is the position of the wave front at time t , which can be expressed as $x_f = d - v_0 t$. In the compressed region charges, which are supposed to be bound to the lattice, are shifted towards the left by a quantity $u(x, t) = -\beta \Delta p (x - x_f)$. In the uncompressed part the charges remain in the original position.

The electric field in the uncompressed part is $E(x, t)$ and $E'(x, t)$ in the compressed part. At the interface between these regions the boundary condition that applies is

$$\varepsilon E(x_f, t) = \varepsilon' E'(x_f, t) \quad (11.31)$$

The boundary condition for the voltage is

$$V(d,t) - V(0,t) = - \int_0^d E(x,t) dx \quad (11.32)$$

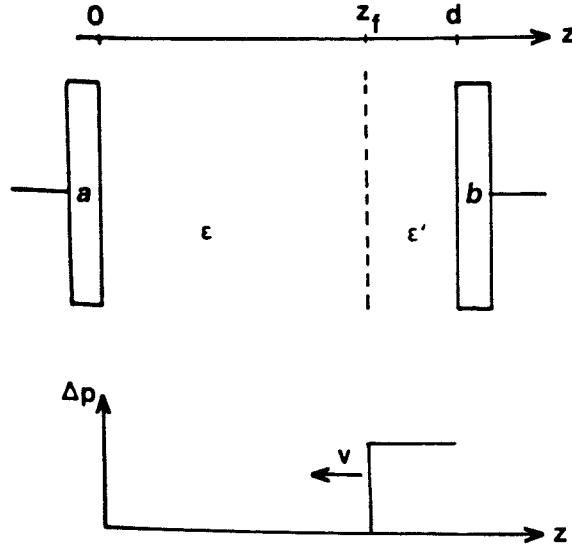


Fig. 11.9 Charge in a dielectric between two electrodes, divided into a compressed region of permittivity ϵ' and an uncompressed region of permittivity ϵ ; the step function compression travels from right to left at the velocity of sound. The position of the wave front is x_f . The undisturbed part has a thickness d_0 (Laurenceau, 1977, with permission of A. Inst. of Phy.).

Laurenceau, et al. (1977) provide the solution for the voltage under open circuit conditions as

$$V(d,t) = \left[1 + \left(\frac{\epsilon}{\epsilon'} \right) (\beta \Delta p - 1) \right] V(x_f, 0) \quad (11.33)$$

The current under short circuit conditions is

$$\frac{1}{A} \int_0^t J(\tau) d\tau = \epsilon \frac{1 + (\epsilon/\epsilon')(\beta \Delta p - 1)}{x_f + (\epsilon/\epsilon')(d - x_f)} V(x_f, 0) \quad (11.34)$$

Equations (11.33) and (11.34) show that the time variation of both the voltage and current is an image of the spatial distributions of voltage and current inside the sample

prior to perturbation. The front of the pressure wave acts as a virtual moving probe sweeping across the thickness at the velocity of sound.

Laurenceau, et al. (1977) proved that the pressure pulse method gives satisfactory results: a compressional step wave was generated by shock waves and a previously charged polyethylene plate of 1 mm thickness was exposed to the wave. The short circuit current measured had the shape expected for a corona injected charge, reversed polarity, when charges of opposite sign were injected. Further, the charges were released thermally and the current was reduced considerably, as expected.

Lewiner (1986) has extended the pressure pulse method to include charges due to polarization P resulting in a total charge density

$$\rho(x) = \rho_s(x) - \frac{dP}{dx} \quad (11.35)$$

where ρ_s is the charge density due to the space charge. The open circuit voltage between the two electrodes is given by

$$V(t) = \beta G(\epsilon_r) \int_0^{x_f} E(x,0) p(x,t) dx \quad (11.36)$$

where $x_f = vt$ is the wave front which is moving towards the opposite with a velocity v , $G(\epsilon_r)$ is a function of the relative permittivity which in turn is a function of pressure. In short circuit conditions the current $I(t)$ in the external circuit is related to the electric field distribution by

$$I(t) = \beta C_0 G(\epsilon_r) \int_0^{x_f} E(x,0) \frac{\partial}{\partial t} p(x,t) dx \quad (11.37)$$

where C_0 is the uncompressed geometric capacitance, $C_0 = \epsilon_0 \epsilon_r A/d$. Equations (11.36) and (11.37) show that if $p(x, t)$ is known, the electric field distribution may be obtained from the measurement of $V(t)$ or $I(t)$. If the pressure wave is a step like function of amplitude Δp (fig. 11-9) then $V(t)$ will be a mirror image of the spatial distribution of the potential in the sample as discovered by Laurenceau, et al. (1977), whereas $I(t)$ is directly related to the electric field. If the pressure wave is a short duration pulse, then $V(t)$ and $I(t)$ give directly the spatial distributions of the electric field and charge density. If the pressure wave profiles change during its propagation through the sample, this effect can be taken into account by a proper description of $p(x, t)$. The techniques used to generate a short rise time pressure waves are shock wave tubes, discharge of capacitors in fluids,

piezoelectric transducers and short rise time laser pulses. Fig. 11.10 shows a typical experimental set up for the laser pulse pressure pulse method.

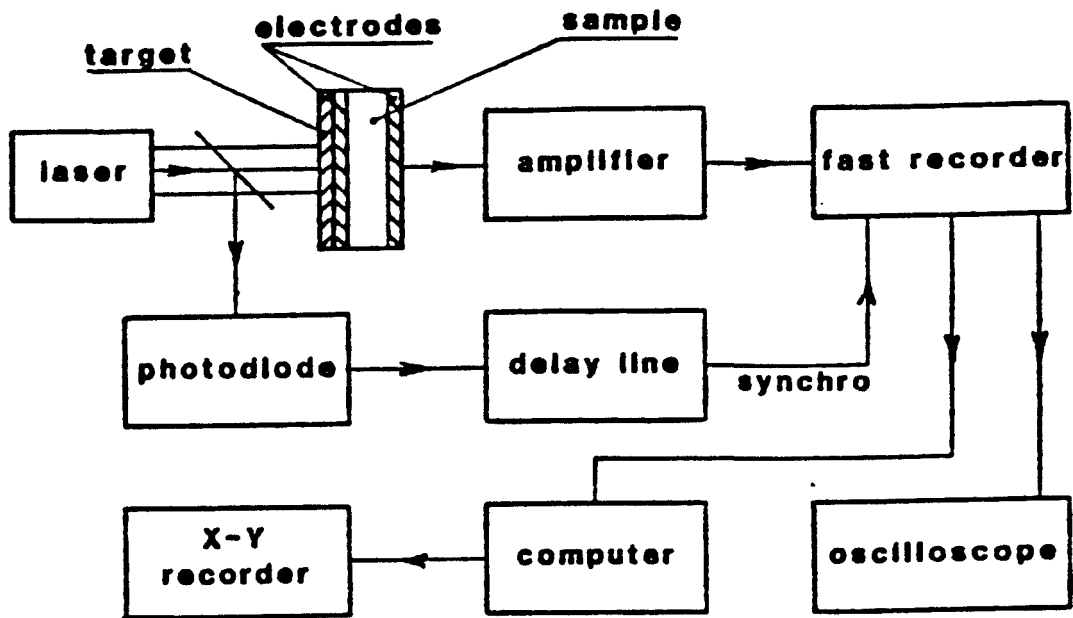


Fig. 11.10 Experimental set up for the measurement of space charge (Lewiner, 1986, © IEEE)

The choice of the laser is governed by two conditions. First, the homogeneity of the beam must be as good as possible to give a uniform pressure pulse over the entire irradiated area. Second, the duration of the laser pulse is determined by the thickness of the sample to be studied. For thin samples, $< 100 \mu\text{m}$, short duration pulses of 0.1-10 ns duration are appropriate. For thicker samples broader pulses are preferred since there is less deformation of the associated pressure pulse as it propagates through the thickness. The power density of the laser beam between 10^6 - 10^8 W/cm^2 yields good results.

The measured voltage and current in $50 \mu\text{m}$ thick Teflon (FEP) film charged with negative corona up to a surface potential is of 1250 V is shown in Fig. 11.11. The charge decay as the temperature of the charged sample is raised. is shown in Fig.11.12. The charged surface retains the charge longer than the opposite surface, and higher temperature is required to remove the charge entirely. The LIPP technique is applied with several variations depending upon the method of generating the pressure pulse. The methods are briefly described below.

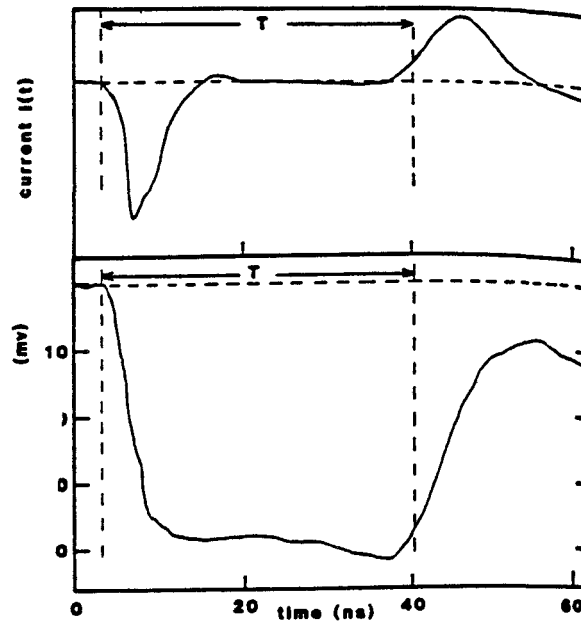


Fig. 11.11 Current and voltage wave forms measured during the propagation of a pressure pulse through a negative corona charged FEP film of $50\text{ }\mu\text{m}$ thickness. T is the time for the pulse to reach the charged surface (Lewiner, 1986, © IEEE).

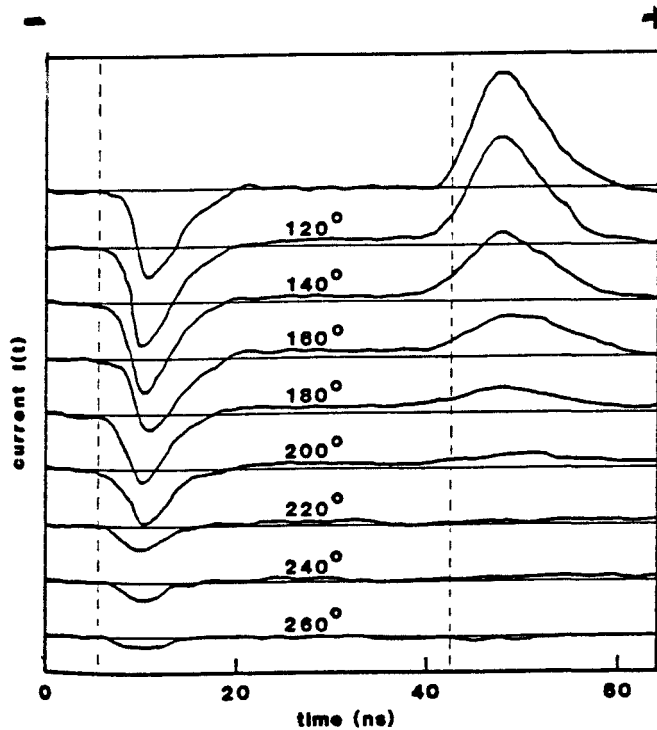


Fig. 11.12 Charge decay with temperature in negative corona charged FEP film. Charged side retains charges longer (LEWINER, 1986, © IEEE)

11.7.1 LASER INDUCED PRESSURE PULSE METHOD (LIPP)

A metal layer on one side of a dielectric absorbs energy when laser light falls upon it. This causes stress effects and a pressure pulse, < 500 ps duration, is launched, which propagates through the sample with the velocity of sound. Fig. 11.13 shows the experimental arrangement used by Sessler, et al.¹⁷. The method uses one sided metallized samples and it is charged at the unmetallized end by a corona discharge. The laser light pulses, focused on the metallized surface, having a duration of 30-70 ps and 1-10 mJ energy, are generated by a Nd:YAG laser.

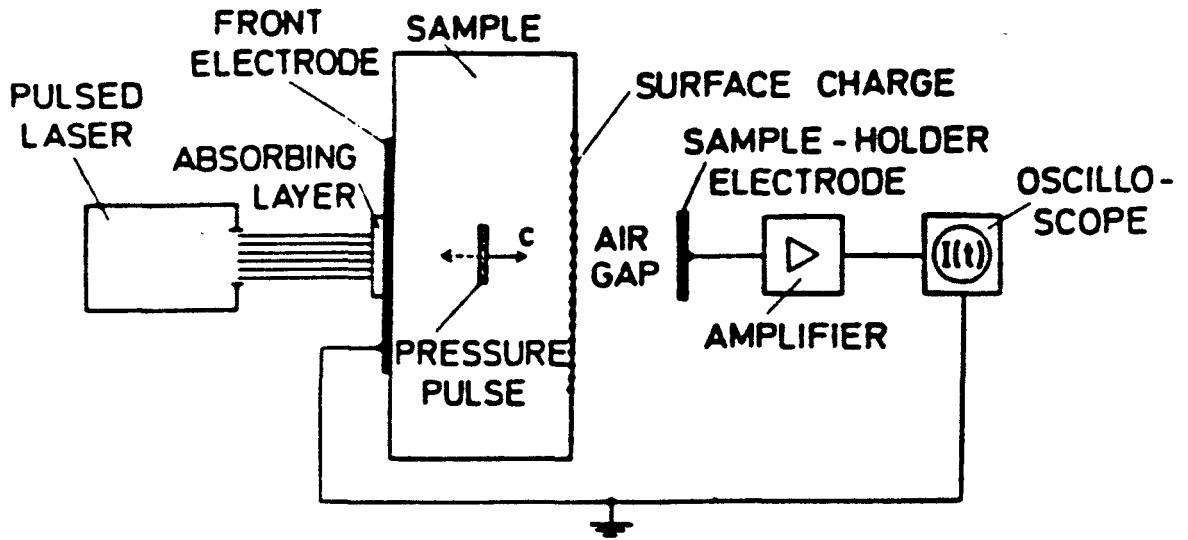


Fig. 11.13 Experimental setup for the laser-induced pressure-pulse (LIPP) method for one sided metallized samples (Sessler, et al., 1986, © IEEE).

The pressure pulse generates, under short circuit conditions, the current signal

$$I(t) = \frac{A p \tau}{\rho_0 (s + \epsilon_s g)} \left[\left(1 + \frac{(\epsilon_\infty + 2)(\epsilon_\infty - 1)}{3\epsilon_s} \right) \rho(x) - \frac{d e(x)}{dx} \right]_{x=vt} \quad (11.38)$$

where A is the sample area, p the amplitude of the pressure, τ the duration of the pressure pulse, ρ_0 the density of the material, s the sample thickness, g the air gap thickness, $e(x)$ the piezoelectric constant of the material, ϵ_s the static (dc) dielectric constant and ϵ_∞ the infinity frequency dielectric constant.

11.7.2 THERMOELASTIC STRESS WAVES

This method has been adopted by Anderson and Kurtz (1984). When some portion of an elastic medium is suddenly heated thermoelastic stress waves are generated. A laser pulse of negligible duration enters a transparent solid and encounters a buried, optically absorbing layer, causing a sudden appearance of a spatially dependent temperature rise which is proportional to the absorbed energy.

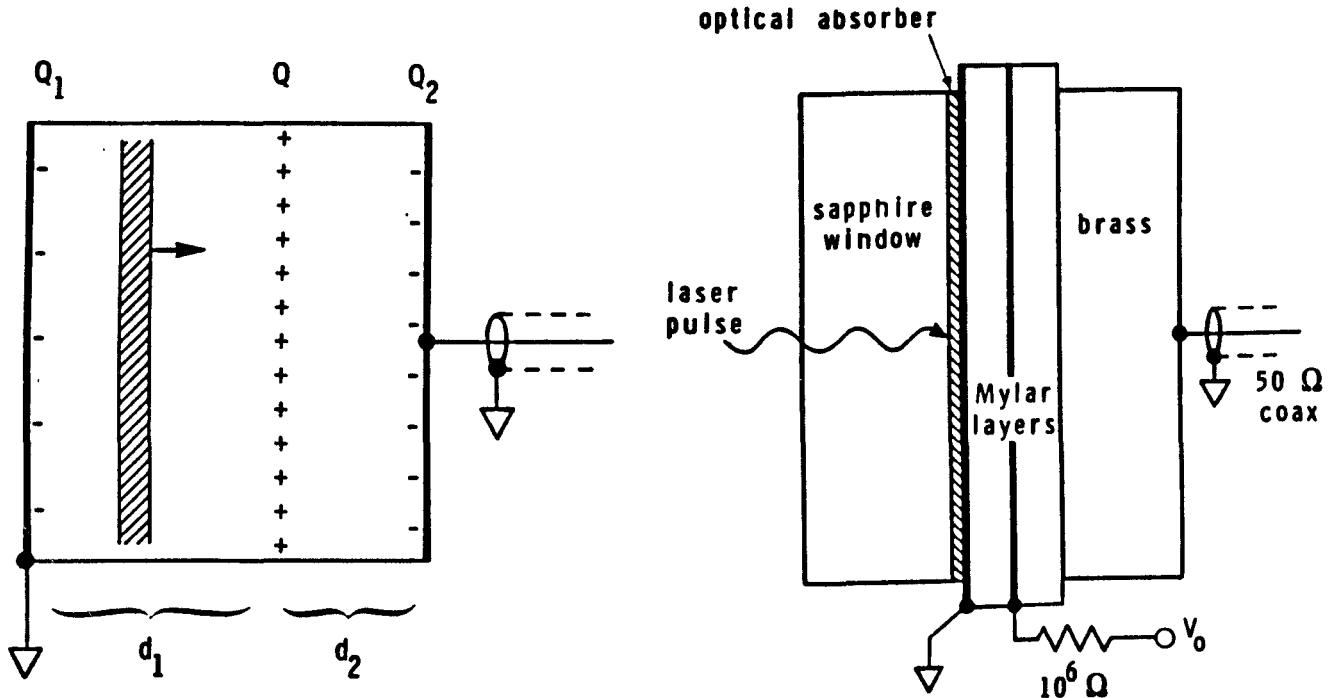


Fig. 11-14 (a) Pressure pulse in a slab of dielectric containing a plane of charge Q . The pulse travels to the right. Electrode 2 is connected to ground through a co-axial cable and measuring instrument. (b) Experimental arrangement for measuring injected space charge. The Mylar film adjacent to the sapphire window acquires internal charge as a result of being subjected to high-field stress prior to installation in the measurement cell. Thicknesses shown are not to scale. (Anderson and Kurtz, 1984 © Am. Inst. Phys.)

The thickness of the sample in the x direction is assumed to be small compared to the dimensions along the y and z directions so that we have a one dimensional situation. At the instant of energy absorption the solid has inertia for thermal expansion and hence compressive stress appears in the solid. The stress is then relaxed by propagation, in the opposite direction, of a pair of planar, longitudinal acoustic pulses which replicate the initial stress distribution. Each of these pressure pulses carries away half of the mechanical displacement needed to relax the heated region. The measured signal is the voltage as a function of time and a deconvolution procedure is required to determine the charge density (Anderson and Kurtz, 1984).

11.7.3 PRESSURE WAVE PROPAGATION (PWP) METHOD

In this method¹⁸ the pressure wave is generated by focusing a laser beam to a metal target bonded to the dielectric sheet under investigation. Earlier, Laurenceau, et al. (1977) had used a step pressure wave to create non-homogeneity as described in section 12.7 above. Though the step function has the advantage that the observed signal is the replica of the potential distribution within the volume before the pressure wave arrived, the difficulty of producing an exact step function limited the usefulness of the method. When a high spatial resolution is required the pulse shape should be small, which is difficult to achieve with a shock tube for two reasons.

First, the shock wave travels in the shock tube with a velocity of a few hundred meters per second; a small angle between the wave front and the sample results in a strong decrease of the spatial resolution. Second, the reproducibility of the wave shape is poor. In the PWP method Alquie, et al. (1981) generalize the calculation to an arbitrary shape of the pressure pulse. The time dependence of the voltage across the sample has a unique solution for the electric field distribution within the sample. Fig. 11.15 shows the sample which has a floating electrode in the middle and two identical samples of FEP on either side. The solution for the electric field shows a sharp discontinuity at the point where there is a charge reversal as expected.

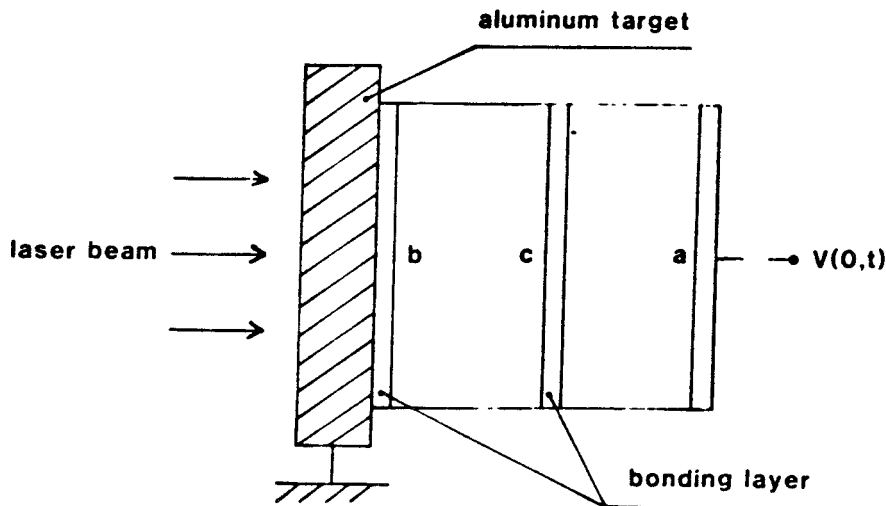


Fig. 11.15 Sample preparation for field distribution study in FEP. Two discs metallized on both sides are joined in the middle creating a floating electrode through which the sample was charged (Alquie, 1981, © IEEE).

11.7.4 NONSTRUCTURED ACOUSTIC PROBE METHOD

The measurement of electric field within a charged foil of relatively small thickness, $\sim 25 \mu\text{m}$ -1mm, offers more flexibility in the choice of methods because the pulses are not attenuated as much as in thicker samples. For larger systems or thicker samples a different approach, in which the electric field is measured by using a nonstructured acoustic pulse to compress locally the dielectric of interest, has been developed by Migliori and Thompson¹⁹. In this technique the pulse shape is unimportant, and attenuation effects are easily accounted for, thereby increasing the effective range of the probe to several tens of centimeters in polymers. Because the probe is sensitive to electric fields, small variations in electric fields and space charge are detectable. Fig. 11.16 shows the experimental arrangement. An acoustic pulse is generated using a spark gap which is located in a tube and situated at about 0.1 mm from a replaceable metal diaphragm. An energy storage capacitor, also located in the same tube (fig. 11.16a) provides the energy for a spark.

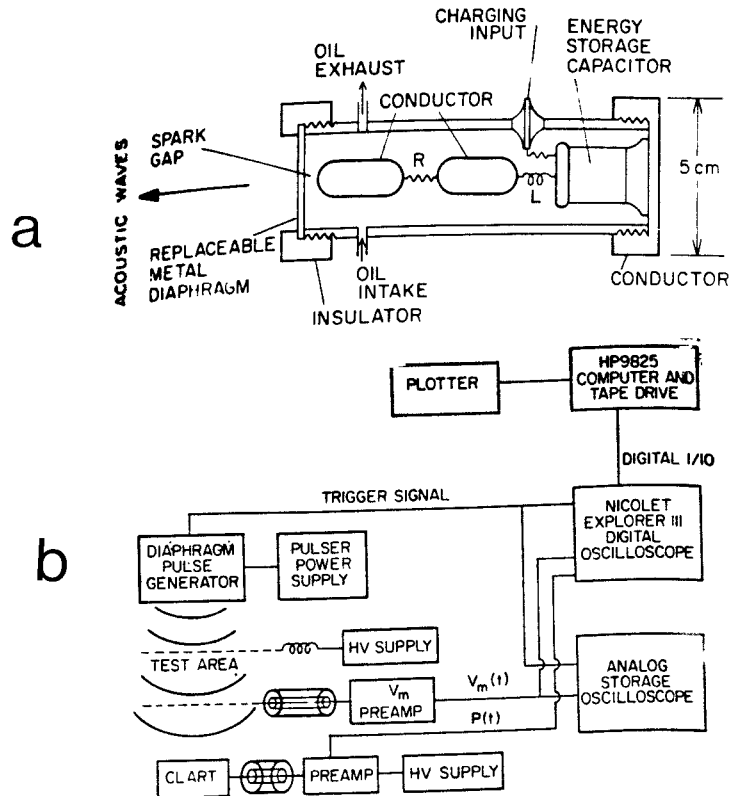


Fig. 11.16. (a) Diaphragm-type acoustic pulse generator used to generate non-structured acoustic pulses for electric field measurements in oil and polymers. (b) Block diagram of the instrumentation used to acquire and process the acoustic and electrical signals required for an acoustic electric field measurement. The box labeled CLART represents the capacitance-like acoustic receiving transducer, and the two pre-amplifiers are described in the text (Migliori and Thompson, 1980, with permission of J. Appl. Phys.).

The other end of the tube is closed with a thick brass plate and the tube is filled with transformer oil. The capacitor is charged until breakdown occurs between the conductor and the metal foil. The spark current ($\sim 100\text{A}$) has a rise time of a fraction of a μs and launches an acoustic wave having a peak amplitude of $\sim 10^5\text{ Pa}$.

The acoustic signal is measured by a capacitance-like acoustic transducer, preamplifier and bias supply immersed in oil in its own tank, which is shielded. This tank is shown as CLART in fig. (11-16b). The measured voltage due to the acoustic pulse is given by

$$V_m(t) = -\left(2 - \frac{1}{\varepsilon}\right) \beta p v \tau E(vt) \quad (11.39)$$

where τ is the time required to pass a particular point. The technique was employed to measure space charge in an oil filled parallel plate capacitor, and 16mm thick poly(methyl methacrylate) (PMMA).

11.7.5 LASER GENERATED ACOUSTIC PULSE METHOD

The non-structured acoustic pulse method described in the previous section has the disadvantage that the generated pulse is not reproducible. It also suffers from insufficient bandwidth and the ratio of low frequency energy to high frequency energy is too high. An improved technique is adopted by Migliori and Hofler²⁰ using a laser to generate the acoustic pulses (Fig. 11.17). Light from a ruby laser which generates pulses of 1.5 J and 15 ns half width is directed through a plate glass window into an aluminum tank filled with liquid freon. The tank contains a laser beam absorber to convert radiation to pressure, a pressure transducer and pre-amplifier, the sample under test and its preamplifier.

The beam strikes an absorber which consists of a carbon paper stretched flat and with the carbon side towards the film. Alignment of the laser perpendicular to the beam is not critical. The paper absorbs radiation and the freon entrained between the paper fibres is heated. The pressure wave has a rise time of about 15 ns and a peak of 0.5 Mpa. The method is sensitive enough to determine the electric fields in the range of 50 kV/m, with a spatial resolution of 50 μm in samples 3 mm thick.

11.7.6 ACOUSTIC PULSE GENERATED BY MECHANICAL EXCITATION

Mechanical excitation may also be used to generate acoustic pulses for probing the electric field within a charged dielectric and this method has been adopted by Roznov and Gromov²¹. A Q-switched ruby laser is used to illuminate a graphite disk with 30 ns pulses and an energy density of 0.5 J/cm^2 .

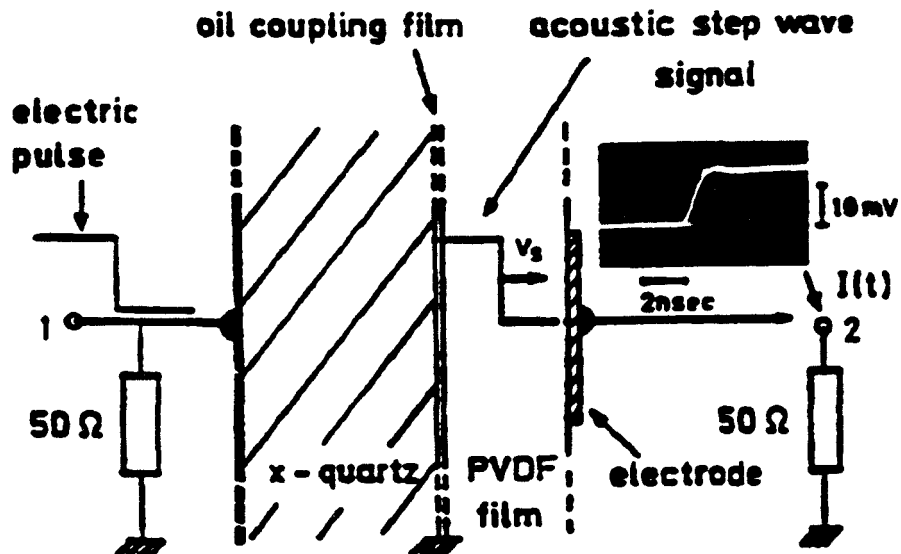


Fig. 11.17 Laser generated acoustic pulse method to measure the electric field inside a solid dielectric (Migliori and Hofler, 1982, with permission of Rev. Sci. Instr.).

11. 7. 7 PIEZO-ELECTRIC PRESSURE STEP METHOD (PPS)

The pressure pulse step method used by Gerhardt-Multhaupt, et al.²² is shown in fig. 11.18. Charging a cable and discharging through a relay-trigger, generates a square pulse of 400-600 V and 100 ns duration. The sequence of the positive and negative pulse is applied to a 3 mm thick piezoelectric quartz pulse. A thin (~ 100 -200 nm) layer of silicone oil couples the generated pressure pulse with the metallized surface of the sample. This sandwich of quartz-oil-sample ensures good acoustic contact. The unmetallized surface is in contact with a conducting rubber disc which is connected to a preamplifier and an oscilloscope. The sample is charged by electron beam of varying energy. This method of charging has the advantage that increasing the energy of the beam can vary the depth of penetration of charges.

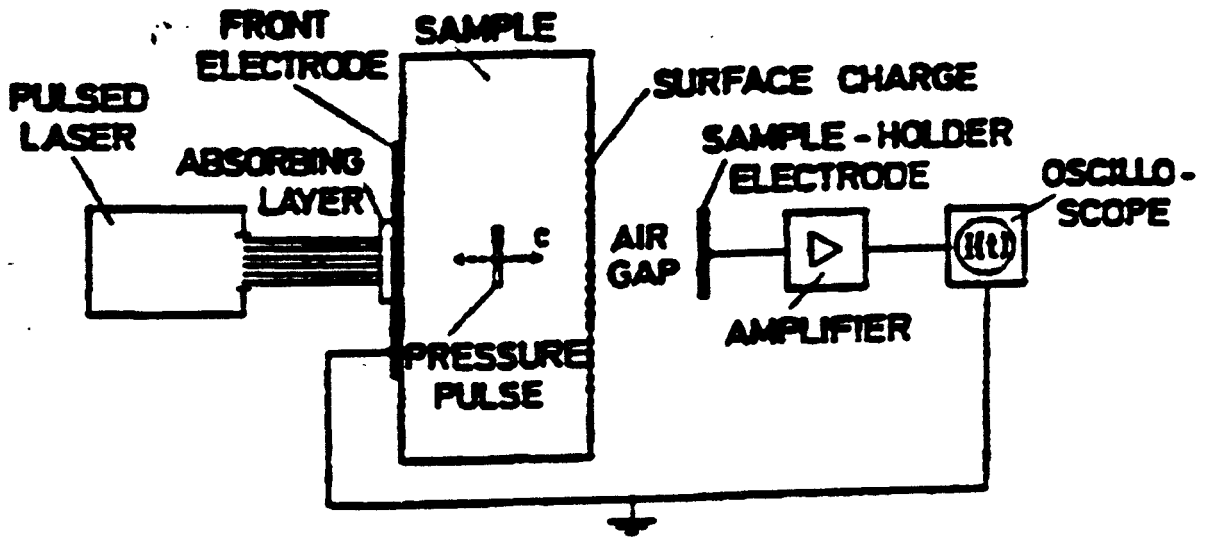


Fig. 11.18 Principle of Piezoelectric pressure step method (PPS) (Sessler²³, 1997, © IEEE).

11.7.8 PULSED ELECTRO-ACOUSTIC STRESS METHOD

The method adopted by Takada and Sakai²⁴ is based on the principle that an electrical pulse applied to a dielectric with a stored charge launches an acoustic pulse that originates from the bulk charge. A dc electric field is applied to deposit charges in the bulk and an ac field of a much smaller magnitude, having 1 MHz frequency, is applied to launch the acoustic wave. The dc supply and ac oscillators are isolated appropriately by a combination of resistance and capacitance.

A piezoelectric transducer is attached to each electrode and the acoustic field excited by the alternating field propagates through the electrodes to the transducer. The electrical signal detected by the transducer is amplified and rectified. The method measures the electric fields in the interface of a dielectric, and utilizes a transducer and associated equipment at each electrode. Further, the signal from the grounded electrode may be measured by directly connecting to a recorder, but the signal from the high voltage electrode needs to be isolated by an optical guide and appropriate data transfer modules.

The technique was improved subsequently by Takada, et al²⁵ whose experimental arrangement is shown in fig. 11.19. The oscillator of the previous method is replaced with a high voltage pulser and the signal from the piezoelectric transducer is recorded on a dual beam oscilloscope for further analysis.

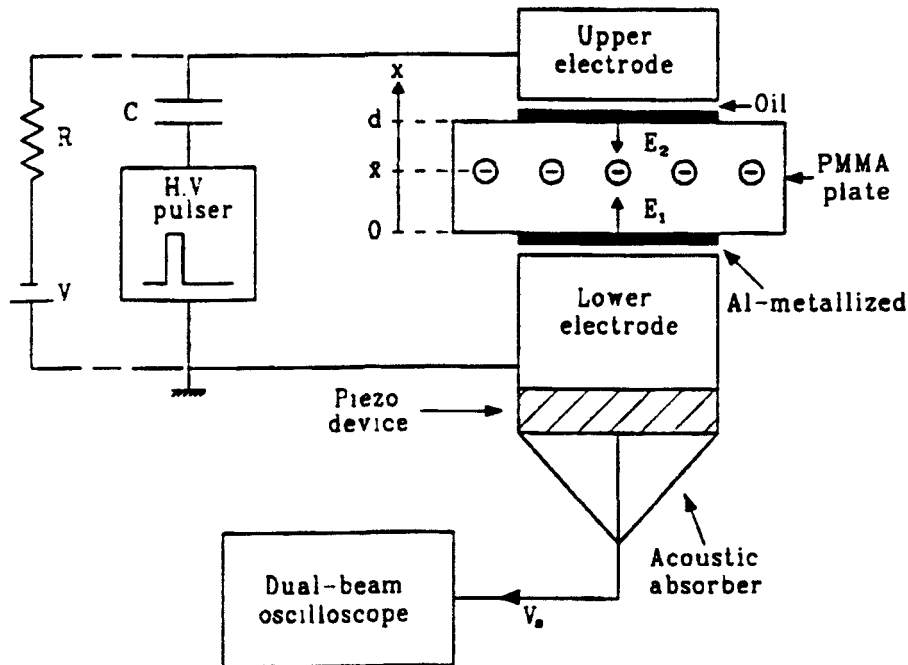


Fig. 11.19 Pulsed Electro-Acoustic Method [Takada et. al., 1987, © IEEE]

11.7.9 ELECTRON BEAM METHOD

This method was used by Sessler, et al. prior to the methods described above²⁶. A mono-energetic electron beam is incident through the front electrode under short circuit conditions (both electrodes connected to ground through small impedance). A brief comment about the method of charging is appropriate here. Arkhipov, et al.²⁷ have shown, by theoretical analysis, that if the rear electrode is grounded and the front (radiated) electrode is open circuited, the space charge build up takes place mostly in the un-irradiated region. For a grounded front electrode, with the rear open circuited, there is only weak charging in the irradiated region. Consequently, a dielectric is much less charged for the second mode than the first.

The beam generates a radiation induced conductivity to a depth determined by its energy. At the plane of the maximum penetration maximum conductivity occurs and the plane is treated as a virtual electrode (thickness $\sim 5\mu\text{m}$). Since the depth of the plane depends on the energy, the virtual electrode may be swept through the dielectric by increasing the energy of the electrons. The currents are measured at each electrode from which the spatial distribution of charges are determined. The method is destructive in the sense that the charge is removed after experimentation.

11.7.10 SPECIAL TECHNIQUES

Techniques dependent on special effects or restricted to selected dielectric materials are described below.

1. Kerr Effect: The Kerr effect, generally applied to birefringent liquids such as nitrobenzene, consists of passing plane polarized light (called a polarizer) through a cell containing the dielectric. The electric field in the dielectric splits the plane polarized light into two components, one component traveling faster than the other. The phase difference between the two components makes the emerging light circularly polarized. This effect is known as the Kerr effect and the intensity of the output light measured by a photomultiplier is dependent on the square of the electric field. The Kerr effect, when it occurs in solids is usually referred to as Pockels effect. This method has been employed by Zahn, et al.²⁸ to study electron beam charged PMMA, having a self field of 1-2.5 MV/m.

2. Spectroscopic Method: In an electric field the spectral lines shift or split and this phenomenon is known as the Stark effect. By observing the spectrum in a spectroscope the field strength may be determined²⁹.

A variation of the Stark effect is to make use of the principle that very weakly absorbed visible monochromatic light liberates carriers that move under the field of trapped charges. By detection of the photocurrent produced one could infer the charge distribution³⁰.

3. Field Probe and Scanning Microscopic Methods: Measurements of an electric field by probes have been used to compute the charge distribution (Tavares, 1973). A scanning microscope has also been used to determine the charging behavior of PMMA under electron beam irradiation³¹.

4. Vapor Induced Depolarization Currents (VIDC): This method is based on the principle that, when a charged dielectric is exposed on one of its faces to a saturated vapor of a solvent, diffusion occurs and the trapped charges are released. A current is detected in the external circuit from which the magnitude of the trapped charge may be evaluated³².

11.8 EXPERIMENTAL RESULTS

The experimental results in fluoropolymers have been succinctly summarized by Sessler (1997), considering different methods of charging and different techniques of measurement. Table 11.3 provides references to selected data. In the following we briefly discuss some polymers of general interest.

Poly(ethylene) (PE): (a) unirradiated

The PEA method has been applied by Mizutani, et al.³³ to study space charge in three different grades of PE at electric field strengths up to 90 MV/m. Homocharges were observed and the space charge was dependent on the electrode material suggesting carrier injection from both electrodes. These results confirm the results of the earlier field probe method adopted by Khalil and Hansen³⁴. To separate injected charges from the ionized impurities, Tanaka, et al. have adopted a technique of charge injection suppression layers³⁵. The pulsed acoustic technique was employed to measure space charge density. In LDPE with suppression layers on both electrodes heterocharges are observed. However, by removing charge suppression homo charges were observed. This technique yields the true charge injected by the electrodes into PE.

In HDPE homocharges are identified at the anode, and in doped HDPE a strong heterocharge, not seen in undoped HDPE, is formed near the cathode (Suzuoki et. al. (1995).

Poly(ethylene) (PE): (b) irradiated

Chen, et al.³⁶ have observed, by LIPP technique, that the energetic ionizing radiations such as a γ -source can alter the chemical structure and may also give rise to the presence of trapped charges. Low radiation doses (≤ 10 kGy) were observed to affect the low density polyethylene differently when compared with high doses (≥ 50 kGy).

A. CROSS LINKED POLYETHYLENE (XLPE)

XLPE is being used increasingly in the power cable industry and two main chemical methods are employed to produce it from low density polyethylene. One method is to use a peroxide (dicumyl peroxide, DCP) which decomposes to form free radicals or a silane based grafting process. The space charge accumulation has been measured by the LIPP technique³⁷ and the observations are:

1. The cross linking method appears to determine the polarity of the space charge adjacent to the electrodes. The DCP cross linking favors heterocharge, and silane cross linking favors homocharge. The charge densities do not vary appreciably.
2. Reversing the applied voltage polarity results in a near-perfect inversion of the space charge across insulator/polymer interface. This is interpreted as evidence for electron transfer by tunneling from donor to acceptor states centered on the Fermi level.

B. FLUOROETHYLENE PROPYLENE (FEP)

The LIPP technique of Sessler et. al. (1977) is applied to FEP, which is charged with electron beams, energy ranging from 10 to 50 keV, as permanent polarization does not occur. Surface charges are observed and very little trapping occurs within the sample volume, in agreement with the results of laser induced acoustic pulse method. Das Gupta, et al.³⁸ have measured the spatial distribution of charges injected by monoenergetic electrons by both LIPP and LIMM techniques and good agreement is obtained between the two methods (Fig. 11.20).

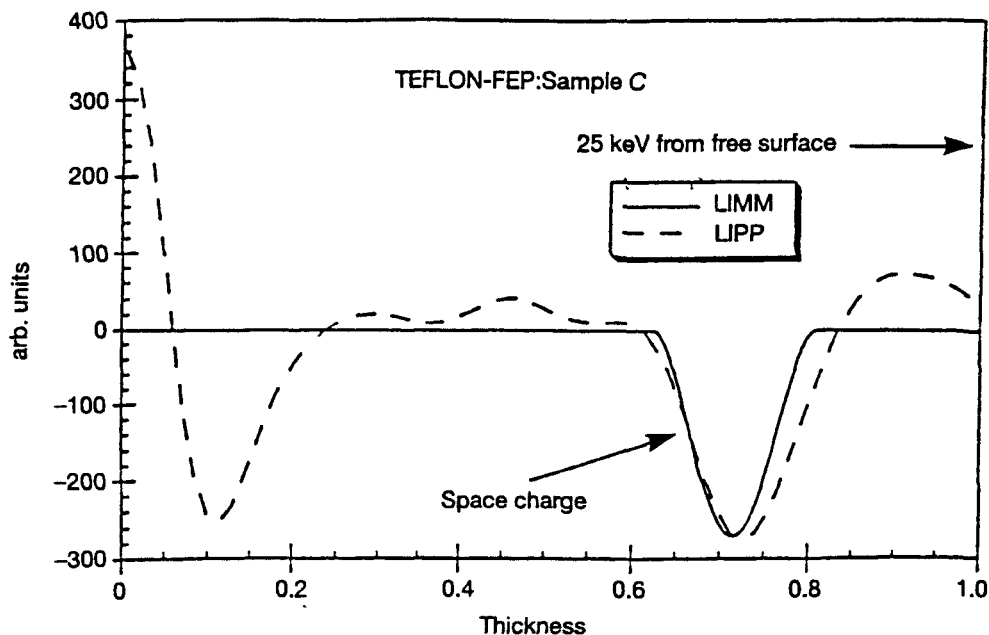


Fig. 11.20 LIPP and LIMM techniques applied to 25 μm FEP with 40 keV electrons from non-metallized side (Das Gupta, et al. 1996, with permission of Inst. Phys., England).

Fig. 11.21 shows the evolution of charge characteristic in FEP charged by electron beam at 120° C. As the annealing duration is increased the charge peak broadens with the charge depth increasing from about 10 μm with no annealing, to about 22 μm with annealing at 120°C. This broadening is caused by charge release at the higher

temperature, charge drift in the self-field extending towards the rear electrode and fast retrapping. The calculated available trap density is $2.5 \times 10^{22} \text{ m}^{-3}$ but the highest filled-trap density in electron beam experiments is $\sim 6 \times 10^{21} \text{ m}^{-3}$ (Sessler, 1977).

In a recent study Bloss, et al.³⁹ have studied electron beam irradiated FEP by using both the thermal pulse (TP) and LIPP method. The TP method has high near-surface resolution, better than 100 nm. The Lipp method has nearly constant resolution with depth. The electron beam deposits a negative charge and in addition, a negative charge layer was formed close to the electrode-polymer interface if the electron beam entered the dielectric through the interface. This effect is attributed to the fact that the metal electrode scatters the electron beam, producing secondary electrons. The secondary electrons have much less energy than the primary ones and do not penetrate deep in to the volume. Since there is no scattering at the unmetallized surface, there are no secondary electrons and only the primary electrons enter the sample.

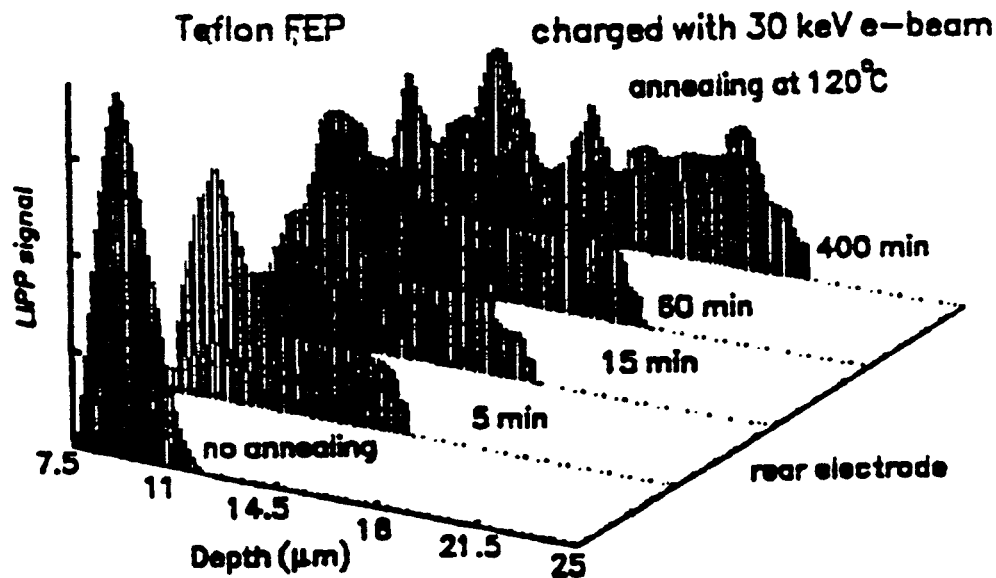


Fig. 11.21 Evolution of charge distribution in 30 keV electron-beam charged Teflon FEP with annealing time at 120°C, as obtained by LIPP method, (Sessler1997, © IEEE).

C. POLY(VINYLIDENEFLUORIDE) PVDF

The LIPP technique of Sessler, et al. (1986) has shown that the piezoelectric material does not form permanent polarization till a threshold electrical field of 100 MV/m is attained. The permanent component of the polarization increases more than proportionally to the voltage, which is characteristic of ferroelectric material. The

permanent polarization is reasonably uniform in the volume, which is typical for high field room temperature poling of PVDF. The same result has also been obtained by the thermal pulse method of De Reggi (1984). The polarization is due to combined effects of instantaneous polarization, electrode charges and space charges accumulated near the electrodes.

D. POLY(TETRAFLUOROETHYLENE)

Corona charged PTFE shows that the trapped charge does not spread as measured by the thermal pulse method. However, PPS measurements of positively and negatively corona charged laminates of the dielectric show that there is some minor spreading towards the electrodes. At high humidity the centroid of the charge has even been observed beneath the sample surface. Positive and negative corona charging at temperatures of 260°C shows a larger and definite bulk charge which is non-uniformly distributed.

11.9 CLOSING REMARKS

As discussed above, a number of methods have been developed for the measurement of space charge in both thin and relatively thick samples (Table 11.3). The method of analyses of the signals have also increased the accuracy of determination of the charge distribution and charge depth. The thermal methods require a deconvolution technique to derive the spatial distribution of charges, $\rho(x)$, from the measured current as a function of time, $I(t)$. The deconvolution may be achieved by the Fourier coefficients of $\rho(x)$. The accuracy of the current measurement limits the number of coefficients to ~ 10 , if the sample is pulsed from both sides (Sessler, et al., 1986).

Table 11.3
Selected Space Charge Measurement in Polymers

The number within square brackets refers to references at the end of the section.

Method	Polymer	Reference
Thermal Pulse Method	Polyethylene	Suzuoki et. al., (1985), ^[40]
	Fluoroethylenepropylene (FEP)	Collins (1980), Bloss et. al. (2000)
DeReggi's Method	PVDF	DeReggi et. al. (1982, 1984) ^[41]
LIMM	Polyethylene	
	Fluoroethylenepropylene (FEP)	Das Gupta et. al. (1996)
	PVDF	Lang and Das Gupta (1981)
Pressure Pulse Method	Poly(ethylene)	Laurenceau (1977)
	PET	Anderson and Kurtz (1984).
Laser Induced Pressure Pulse Method (LIPP)	Fluoroethylenepropylene	Alquie et. al. (1981), Lewiner (1986), Das Gupta et. al. (1996)
	PVDF	Sessler (1997)
	Polyimide (Kapton)	Sessler (1997)
	PET (Mylar)	Sessler (1997)
	Cross linked polyethylene (XLPE)	Bambery and Fleming (1998)
	Polyethylene	Lewiner (1986), ^[42]
	PET	Sessler (1997)
Thermoelastic Stress Waves	PET	
Pressure Wave Propagation (PWP) Method	Fluoroethylenepropylene	
Nonstructured Acoustic Probe method	PMMA	Migliori and Thompson (1980)
Mechanically generated acoustic Probe Method	PMMA	Rozno and Gromov (1986)
	Polyethylene	Rozno and Gromov (1986)

Table 11.3 Continued

Method	Polymer	Reference
Piezoelectric Pulse Step (PPS)	Fluoroethylenepropylene	Gerhard-Multhaupt et. al. (1983)
	Mylar	Gerhard-Multhaupt et. al. (1983)
	P(VDF-TFE)	[43]
Pulsed Electro-acoustic Stress Method	PE, PET, PS, PVDF, XLPE,	(Takada et. al. 1983), [44], [45]
	LDPE	Tanaka et. al. (1995)
	PMMA	[46]
Electron beam sweeping	FEP	Sessler et. al. (1977)
Kerr Effect	PMMA	Zahn et. al. (1987)
Field Probe	LDPE	Khalil et. al. (1988)

The thermal methods have the advantage of a high depth resolution for thickness less than $\sim 100\mu\text{m}$. The acoustic methods have the advantages of a good resolution throughout the bulk ($\sim 1\text{-}2\ \mu\text{m}$). The Thermal Pulse method, LIMM, LIPP and PEA are being increasingly used in preference to other methods. It is now possible to measure the space charge by more than one technique and these complementary measurements have been carried out in FEP, using the LIMM and LIPP techniques (Das Gupta et. al., 1996), and LIPP and TP methods (Bloss, et al. 2000). Such techniques help to isolate experimental artifacts from the characteristics of the dielectric under study.

Damamme, et al.⁴⁷ have discussed the points to which attention should be paid in calibrating the experimental setup. Calibration generally falls into two broad categories: one, the parameters that are associated with the charging method, charge, potential, temperature, energy of injected electrons and their total charge, etc. The latter may be measured to an accuracy of $\pm 1\ \text{pc}$. The charge response resolution is $\sim 2\ \text{fC}$ but it may be particularly difficult to achieve this accuracy in case of short laser pulses. The second is connected with the measurement technique used. The analyses of measurements require several physical properties of the polymer, such as the speed of sound, the thermal diffusivity, the permittivity, the high frequency dielectric constant, etc. These properties should be measured in situ, preferably, to remove ambiguity in their values. Since a host of experimental techniques are required it may not always be possible to accomplish this. In such situations the properties obtained for the same sample with particular reference to humidity, previous history, etc. should be used.

The role of the space charge in the performance characteristics of dielectrics has been discussed by Bartnikas⁴⁸ in both communication and power application areas. Future work should be concentrated on establishing a clear connection between charging characteristic and operational performance in the technological applications.

11.10 REFERENCES

- ¹ J. Lewiner, IEEE Trans. on EI, **12** (1986) 351.
- ² G. Blaise and W. J. Sarjeant, "IEEE Trans. on Diel. El., **5** (1998) 779.
- ³ H. Frölich, "Introduction to the theory of the polaron", in "Polarons and Excitons", Eds : C. G. Kwyer and G. D. Whitefield, : Oliver & Boyd, London, 1963.
- ⁴ B. Gross, IEEE Trans. on Nucl. Sci., **NS-25** (1978) 1048.
- ⁵ B. Gross, J. Dow, S. V. Nablo, J. Appl. Phys., **44** (1973) 2459.
- ⁶ B. Gross, G. M. Sessler, J. E. West, Appl. Phys. Lett., **22** (1973) 315.
- ⁷ S. Osaki, S. Uemura, Y. Ishida, J. Poly. Sci. A-2, **9** (1971) 585.
- ⁸ N. H. Ahmed and N. N. Srinivas, IEEE Trans. Diel. El., **4** (1997) 644.
- ⁹ R. E. Collins, J. Appl. Phys., **51** (1980) 2973.
- ¹⁰ H. Von Seggern, Appl. Phys. Lett., **33** (1978) 134.
- ¹¹ A. S. DeReggi, C. M. Guttman, F. I. Mopsik, G. T. Davis and M. G. Broadhurst, Phys. Rev. Lett., **40** (1978) 413.
- ¹² F. I. Mopsik, and A. S. DeReggi, J. Appl. Phys., **53** (1982) 4333; Appl. Phys. Lett., **44** (1984) 65.
- ¹³ Y. Suzuoki, H. Muto, T. Mizutani, J. Appl. Phys., **24** (1985) 604.
- ¹⁴ S. B. Lang and D. K. Das Gupta, Ferroelectrics, **39** (1981) 1249.
- ¹⁵ P. Laurenceau, G. Dreyfus, and J. Lewiner, Phys. Rev. Lett., **38** (1977) 46.
- ¹⁶ R. A. Anderson and S. R. Kurtz, J. Appl. Phys., **56** (1984) 2856.
- ¹⁷ G. M. Sessler, R. Gerhardt-Mulhaupt, von Seggern and J. W. West, IEEE Trans. Elec. Insu., **EI-21**, (1986) 411.
- ¹⁸ C. Alquié, G. Dreyfus and J. Lewiner, Phys. Rev. Lett., **47** (1981) 1483.
- ¹⁹ A. Migliori and J. D. Thompson, J. Appl. Phys., **51** (1980) 479.
- ²⁰ A. Migliori and T. Hofler, Rev. Sci. Instrum., **53** (1982) 662.
- ²¹ A. G. Rozno and V. V. Gromov, IEEE Trans. Elec. Insul., **EI-21**, (1986) 417-423
- ²² R. Gerhardt-Mulhaupt, M. Haardt, W. Eisinger and E. M. Sessler, J. Phys. D: Appl. Phys., **16** (1983) 2247.
- ²³ G. M. Sessler, IEEE Trans. Diel. Elec. Insu. **4** (1997) 614.
- ²⁴ (a) T. Takada and T. Sakai, IEEE Trans. Elec. Insu., **EI-18**, (1983) 619.
(b) T. Takada, IEEE Trans. Diel. Elec. Insul., **6** (1999) 519.
- ²⁵ T. Takada, T. Maeno and Kushibe, IEEE Trans. Elec. Insul., **22** (1987) 497.
- ²⁶ G. M. Sessler, J. E. West, D. A. Berkeley and G. Morgenstern, Phys. Rev. Lett., **38** (1977) 368.
- ²⁷ V. I. Arkhipov, A. I. Rudenko and G. M. Sessler, J. Phys. D: Appl. Phys., **24** (1991) 731.

-
- ²⁸ M. Zahn, M. Hikita, K. A. Wright, C. M. Cooke and J. Brennan, IEEE Trans. Elec. Insu., **22** (1987) 181.
- ²⁹ S. J. Sheng and D. M. Hanson, J. Appl. Phys., **45** (1974) 4954.
- ³⁰ A. D. Tavares, J. Chem. Phys., **59** (1973) 2154.
- ³¹ Z. G. Song, H. Gong and C. K. Ong, J. Appl. Phys., **30** (1997) 1561.
- ³² M. Falck, G. Dreyfus, and J. Lewiner, Phys. Rev., **25** (1982) 550.
- ³³ T. Mizutani, H. Semi and K. Kaneko, IEEE Trans. Diel. Elec. Insul., **7** (2000) 503.
- ³⁴ M. S. Khalil, B. S. Hansen, IEEE Trans. Elec. Insu., **23** (1988) 441.
- ³⁵ Y. Tanaka, Y. Li, T. Takada and M. Ikeda, J. Phys. D: Appl. Phys., **28** (1995).
- ³⁶ G. Chen, H. M. Banford, A. E. Davies, IEEE Trans. Diel. Elec. Insul., **5** (1998) 51.
- ³⁷ K. R. Bambery and R. J. Fleming, IEEE Trans. Diel. Elec. Insul., **5** (1998) 103.
- ³⁸ D. K. Das Gupta, J. S. Hornsby, G. M. Yang and G. M. Sessler, J. Phys. D: Appl. Phys., **29** (1996) 3113.
- ³⁹ P. Bloss, A. S. DeReggi, G. M. Yand, G. M. Sessler and H. Schäfer, J. Phys. D: Appl. Phys., **33** (2000) 430.
- ⁴⁰ A. Cherfi, M. Abou Dakka, A. Toureille, IEEE Trans. Elec. Insu. **27** (1992) 1152.
- ⁴¹ M. Wübbenhorst, J. Hornsby, M. Stachen, D. K. Das Gupta, A. Bulinski, S. Bamji, IEEE Trans. Diel. Elec. Insul., **5** (1998) 9.
- ⁴² T. Mizutani, IEEE Trans. Diel. Elec. Insul., **1** (1994) 923.
- ⁴³ S. N. Fedonov, A. E. Sergeeva, G. Eberle and W. Eisenmenger, J. Phys. D: Appl. Phys., **29** (1996) 3122.
- ⁴⁴ Y. Li, M. Yasuda, T. Takada, IEEE Trans. Diel. Elec. Insul., **1** (1994) 188.
- ⁴⁵ X. Wang, N. Yoshimura, Y. Tanaka, K. Murata and T. Takada, J. Phys D: Appl. Phys., **31** (1998) 2057.
- ⁴⁶ T. Maeno, T. Futami, H. Kushibe, T. Takada and C. M. Cooke and J. Brennan, IEEE Trans. Elec. Insul., **23** (1988) 433.
- ⁴⁷ G. Damamme, C. Le Gressus and A. S. De Reggi, IEEE Trans. Diel. Elec. Insu., **4** (1997) 558.
- ⁴⁸ R. Bartnikas, Trans. Diel. Elec. Insul. **4**, (1997) 544.

APPENDIX 1

TRADE NAMES OF POLYMERS

<u>Chemical name</u>	<u>Trade name</u>	<u>Formula</u>	<u>Remarks</u>
Poly(tetrafluoroethylene)	Teflon PTFE Halon fluon	$(\text{CF}_2\text{-CF}_2)_x$	rods, sheets, Film, extrusion
Poly(fluoroethylene-propylene)	Teflon FEP	$(\text{CF}_2\text{-CF}_2)_x (\text{C}_3\text{F}_6)_y$	Film, molding and extrusion
Poly(3-perfluoropropoxy-perfluorohexamethylene)	Teflon PFA	$(\text{C}_2\text{F}_4)_x (\text{C}_2\text{F}_3\text{O})_y \text{C}_3\text{F}_4$	Film, extrusion
Poly(ethylene terephthalate) (PET) Aromatic polyamide	Mylar	$(\text{CO}_2 \text{C}_6\text{H}_6 \text{CO}_2 \text{C}_2\text{H}_4)_x$	Film, tubing
Polyimide (PI)	Nomex, Kevlar	$(\text{NH C}_6\text{H}_6 \text{NH CO C}_6\text{H}_6 \text{CO})_x$	Paper, laminates
	Kapton Upilex Pyre-ML	$[(\text{C}_6\text{H}_6)_3 \text{O} (\text{C}_2\text{NO}_2)_2]_x$	Film, enamel, resin
Polyetherimide (PEI)	Ultem	$[(\text{C}_2 \text{NO}_2)_2 (\text{C}_6\text{H}_6)_5 \text{O} \text{C}_3\text{H}_6]_x$	Film, molding resin
Poly(methyl methacrylate) (PMMA)	Perspex Acrylic Lucite Acrylite Plexiglas	$(\text{C}_5 \text{H}_8 \text{O}_2)_x$	molding resin, sheets

<u>Chemical name</u>	<u>Trade name</u>	<u>Formula</u>	<u>Remarks</u>
ethylene tetrafluoroethylene (ETF)	Tefzel	$(C_4H_4F_4)_x$	Film, extrusion
Polyetherketone	PEEK	$[(C_6H_6)_3 C_2O_3]_x$	molding resin
Polyvinylidene fluoride (PVDF)	Kynar	$(C_2 H_2 N)_n$	Film,
Polychlorotrifluoroethylene (PCTFE)	Kel-F	$(C_2 F_3 Cl)_n$	Film, extrusion
Polystyrene-butadiene	K-resin		molding resin
Polycarbonate (PC)	Lexan, Calibre, Makrolon	$H [(C_6H_6)_2 C_4H_6O_3]_n OH$	Molding compound
Polybutylene Terephthalate (PBT) or Polytetramethylene terephthalate (PTMT)	Ultradur Valox Celanex	$[(C_6H_6) C_6 O_4 H_8]_n$	Molding Resin
Nylon	Capron, Rilsan, Ultramid, Celanese, Zytel and Vydine	$[C_{12}H_{22}O_2N_2]_n$	Molding Resin, extrusion, enamel
Polysulfone	Udel, Ultrason S	$[(C_6H_6)_4 C_3H_6 O SO_2]_n$	Molding resin
Phenol formaldehyde	Bakelite	$[(C_6H_6)_4 C_3 O_3 H_8]_n$	Resin, Laminate
Polyester-imide (PEI)	Teramid Isomid	$[(C_6H_6)_4 C_{18} H_8 O_{18} N_8]$	enamel

APPENDIX 2

General Classification of Polymer Dielectrics

<u>Thermoplastic</u>		<u>Elastomers</u>	<u>Thermosetting</u>	<u>Ceramic/glass</u>
RESINS	Films			
Acetal	Cellulose Acetate (CA)	Natural rubber (polyisoprene)	Alkyds or thermosetting polyester	Alumina
Acrylic		Butyl rubber	Allyls	Aluminum nitride
Amide (Nylon)	Cellulose triacetate	Styrene Butadiene Rubber	Aminos	Aluminum silicate
Polyetherimide	PTFE	Neoprene	Epoxy	Beryllia
Polyarylate	PFA	EPDM	Phenolics	Boron nitride
Polybutylene	FEP	EPR		Cordierite
Terephthalate				
Polycarbonate	ETFE	chlorosulfonated polyethylene (CSM)		Diamond
Polyetheretherketone	ECTFE	Chlorinated polyethylene (CP)		Magnesia
Polyethylene ether	PVDF			Porcelain
Polyphenylene	PCTFE			Sapphire
Polypropylene	PC			Silica
Polystyrene	PET			Steatite
Styrene-Butadiene	PE			Zircon

<u>Thermoplastic</u>	<u>Elastomers</u>	<u>Thermosetting</u>	<u>Ceramic/glass</u>	<u>Thermoplastic</u>
Styrene acrylonitrile	PI			
Acrylonitrile	PPA			
butadiene styrene				
Polysulfone	PP			
Polyether sulfone	PS			
	PVC			
	PS			
	PES			
	PEI			

APPENDIX 3

Selected Properties of Insulating Materials

E = Dielectric Strength (MV/m), * indicates short term

ρ = Volume Resistance, Ω m

$\tan \delta$ values should be multiplied by 10^{-4} , i.e. 40 means 0.004

Material	E	ρ	ϵ (50/60 Hz)	ϵ (1 kHz)	ϵ (1 M Hz)	$\tan \delta$ (50/60 Hz)	$\tan \delta$ (1 kHz)	$\tan \delta$ (1 M Hz)
Acetol (homopolymer)	15	1×10^{13}	3.7	-	3.7	-	-	48
Acetol, (co-polymer)	15	1×10^{12}	3.7	-	3.7	10	-	10
Acrylonitrile butadiene styrene (ABS)	17 ¹ *	2×10^{14}	2.6	-	2.6	40	-	60
Cellulose Acetate	160*	10^{13}		3.6	3.2	-	130	380
Polyethylene (PE)	40-60	10^{14}	2.3	2.3	2.3	2-10	2-10	2-10
Polyethylene (LD)	200*	10^{14}	2.3	2.2	2.2	2-10	3	3
Polyethylene (HD)	200	10^{14}	2.35		2.34	2.4	-	2-7
Polyethylene (XL)	220	10^{14}			2.3	-	-	3
Polypropylene (PP), (Unoriented)	-	3×10^{13}	2.27	2.2	2.2	4	3	3
Polypropylene (PP), (Biaxially oriented)	200*	3×10^{12}	2.27	2.2	2.2	-	3	3
Polypropylene/polyeth ylene copolymer	24	4×10^{13}			2.24			3
Polystyrene (PS)	200*	10^{14}	2.6	2.4-2.7	2.4-2.7	3	5	5
Polyvinyl chloride (PVC), (plasticized)	72	10^{12}	-	4-8	3.3-4.5	-	700- 1600	400-1400

¹ *Handbook of Electrical and Electronic Insulating Materials*: W. T. Shugg, IEEE Press, 1995.

APPENDIX 3 (Contd.)

Material	E	ρ	ϵ (50/60 Hz)	ϵ (1 kHz)	ϵ (1 M Hz)	$\tan \delta$ (50/60 Hz)	$\tan \delta$ (1 kHz)	$\tan \delta$ (1 M Hz)
Polyvinyl chloride (PVC)	40	10^{13}	3.4	3.4	3.1	200	180	150
Polymethyl methacrylate (PMMA)	16-20	1×10^{16}	3.7-4.0	3.5	2.2	500	500	300
Polytetra fluoroethylene (PTFE)	88-176	10^{16}	2.1	2.0	2.0	2	1	1
Teflon-PFA	176-200	10^{16}	-	2.0	2.0	-	2	2
Teflon-FEP	200	10^{16}	-	2.0	2.0	-	2	3
Teflon-ETFE	200			2.6	2.6	-	80	5
PVDF	10.2	2×10^{12}	-	8.4	6.6	-	180	1700
ECTFE	200-225	10^{14}	-	2.6	2.6	-	20	130
PCTFE	120-156	10^{16}	-	2.6	2.3	210 (100 Hz)	230	120
Polycarbonate (PC)	252	10^{14}	-	3.0	2.9	-	15	100
Polyester (PET)	275-300	10^{16}		3.2	3.0	-	50	160
Polyimide (PI)	280	10^{16}	-	3.5	3.4	-	25	100
Polyphenylene sulphide (PPS)	15.2	10^{14}	3.1	-	3.2	3	-	7
Polyphenylene ether (PPE)	22	10^{14}	2.6	-	2.6	4	-	9
Nylon 6/6	24	10^{11}	8.0		4.6	2000		1000
Nylon 11	30	10^{12}	3.9		3.1	400		500
Polyetherimide(PEI)	19	7×10^{15}	3.2		3.1	40		60

APPENDIX 3 (Contd.)								
Material	E	ρ	ϵ (50/60 Hz)	ϵ (1 kHz)	ϵ (1 M Hz)	$\tan \delta$ (50/60 Hz)	$\tan \delta$ (1 kHz)	$\tan \delta$ (1 M Hz)
Polybutylene Terephthalate (PBT)	17	4×10^{14}	3.3	3.2-3.3 (100 Hz)	3.1	20		200
Polysulfone (PS)	17	1×10^{15}	3.1		3.0	8		34
Poly(ether sulfone) (PES)	16	$>1 \times 10^{15}$	3.5	3.5	3.5	10	35	40
Epoxy resin	25-45	10^{13} - 10^{15}	3.5-3.9	-	3.6	35-90	-	150-200
Glass Filled Alkyd/Polyester resin	15	10^{11}	5.6	-	4.6	1000	-	200
Glass filled Melamine Molding resin	12	2×10^9	8.0		6.2	-	-	200
Glass Filled Epoxy Molding Resin	15	1×10^{11}	5.0	-	4.6	100	-	100
Natural Rubber (hard)	15-40	1×10^{14}	3.2-4	-	2.5-3.5	30-150	50-150	-
Natural Rubber (soft)	15-50	-	3.5-5	-	-	20-800	-	-
Butyl Rubber	24	10^{15}	2.1-2.4	-	-	-	30	-
Neoperene	16-28	1×10^9	6-8	-	-	-	30	-
Styrene Butadiene Rubber (SBR)		1×10^{13}	3.0-3.5				30	
Ethylene propylene diene rubber (EPDM)	20-	1×10^{14}	2.5-3.5	-	-	-	70	-
Silicone Rubber	20-30		2.5-3.2	2.5-3.2	3.0-3.6	4-25	3-10	20-50
Polyurethane	20	4×10^9		10	8		800	1000
Silicone resin	22	2×10^{12}	2.7		2.7	10		10

APPENDIX 3 (Contd.)								
Material	E	ρ	ϵ (50/60 Hz)	ϵ (1 kHz)	ϵ (1 M Hz)	$\tan \delta$ (50/60 Hz)	$\tan \delta$ (1 kHz)	$\tan \delta$ (1 M Hz)
Aramid Paper (Calendered)			2.4			60		
Aramid Paper (uncalendered)			1.3				30	
Aramid and mica paper			3.6			1200		
Alumina ceramic	12.5	1×10^{12}			8.8-10			20
Beryllia ceramics	12	1×10^{12}			7.0			50
Glass bonded mica	16	1×10^{10}			6.7			18

CERAMICS

(Reproduced : Handbook of Electrical and Electronic Insulating Materials, II ed. W. T. Shugg, IEEE)

Material	Dielectric strength (MV/m)	Dielectric constant (1 MHz)	$\tan \delta$ (1 MHz) $\times 10^4$
Alumina (99.9% Al_2O_3)	13.5	10.1	2
Aluminum silicate	6	4.1	27
Beryllia (99% BeO)	14	6.4	1
Boron nitride	38	4.2	3.4
Cordierite	200	4.8	50
Magnesia	-	5.4	< 3
Porcelain	-	8.5	50
Quartz	-	3.8	38
Sapphire	-	9.3-11.5	0.3-8.6
Silica (fused)	-	3.2	45 @ 10GHz
Steatite	9-16	5.0	23

APPENDIX 3 (Contd.)			
Material	Dielectric strength (MV/m)	Dielectric constant (1 MHz)	$\tan \delta$ (1 MHz) $\times 10^4$
Zircon	-	5.0	23

MICA and MICA PRODUCTS

(Reproduced : Handbook of Electrical and Electronic Insulating Materials, II ed. W. T. Shugg, IEEE)

Material	Dielectric strength (MV/m)	Dielectric constant (1 MHz)	$\tan \delta$ (1 MHz) $\times 10^4$
Muscovite Ruby (natural)	120	6.5-8.7	-
Phlogopite amber (natural)	120	5-6	-
Fluoro-phlogopite synthetic	120	6.5	2
Glass bonded mica	14-16	6.7-12.5	12-60

REFERENCES

1. W. T. Shugg, "Handbook of Electrical and Electronic Insulating Materials, IEEE Press, 1995.
2. C. C. Ku and R. Liepins, "Electrical Properties of Polymers", Hanser Publishers, Munich, 1987.
3. A. Von Hippel, "Dielectric Materials and Applications", The Technology Press of M. I. T. and John Wiley and Sons, New York, 1958.
4. F. E. Karasz, Ed., "Dielectric Properties of Polymers", Plenum Press, New York, 1972.
5. Vishn Shah, "Handbook of Plastics Testing Technology", Wiley-Interscience, New York, 1984.
6. J. Arganoff, Ed., Modern Plastics Encyclopedia, Vol. 60, McGraw Hill, New York, (1983-84).

APPENDIX 4

Relative Ranking of Thermoplastic Polymers

1= Most desirable, 18= Least desirable

POLYMER	Dielectric strength	Dielectric constant	Dissipation factor	Volume resistivity	Arc resistivity
Acetal homo-polymer	15	14	7	15	4
Acetal copolymer	15	14	8	16	2
Acrylic	5	13	17	1	1
Nylon 6/6	1	18	18	18	7
Nylon 11	8	16	16	16	9
Polyamide-imide	3	17	15	5	3
Polyetherimide	7	10	11	2	8
Polybutylene terephthalate	11	11	10	7	5
Polycarbonate	15	9	14	4	11
Modified polyphenylene oxide	15	8	2	12	18
Polyphenylene sulfide	15	8	2	12	18
Polypropylene	1	1	4	9	6
Polystyrene	5	2	1	9	16
Polystyrene butadiene	12	2	9	12	17
Styrene acrylonitrile	8	4	13	9	12
Acrylonitrile butadiene styrene	8	4	12	8	13
Polysulfone	8	7	5	6	10
Polyethersulfone	12	12	6	3	15

Handbook of Electrical and Electronic Insulating Materials, W. T. Shugg, IEEE©, 1995

APPENDIX 5

SELECTED PROPERTIES OF POLYMER INSULATING MATERIALS

POLYMER	Recommended Temp (°C)	Volume resistivity (Ωm)	Arc resistance (s)
Acetal homo-polymer ¹	90	1×10^{13}	220
Acetal copolymer ¹	105	1×10^{14}	240 (burns)
Acrylic ¹	95	1×10^{16}	no tracking
Acrylonitrile butadiene – styrene ¹	95	2×10^{14}	100
Epoxy, Bisphenol A			100^3
Modified polyphenylene – oxide ¹	105	1×10^{14}	75
Nylon 6/6 ¹	130	1×10^{13}	130
Nylon 11 ¹	65	1×10^{14}	123
Polyamide-imide ¹	260	8×10^{14}	230
Polybutylene terephthalate ¹	150	4×10^{14}	184
Polycarbonate ¹	115	8×10^{14}	120
Polyetherimide ¹	170	7×10^{15}	128
Polyethersulfone ¹	180	$>1 \times 10^{15}$	70
Polyethylene, LD	80	1×10^{14}	160^2

Polyethylene, HD	90	1×10^{14}	235
Polyimide, unreinforced	240	1×10^{16}	152-230 ³
Polyphenylene sulfide ¹	205	1×10^{14}	34
Polypropylene ¹	105	$>1 \times 10^{14}$	150
Polystyrene ¹	70	1×10^{14}	65
Polysulfone ¹	150	5×10^{14}	122
Poly(tetrafluoroethylene)	260	$>1 \times 10^{16}$	$>200^3$
Poly(trifluorochloroethylene)	200	$>1 \times 10^{16}$	$>360^3$
PVC	80	1×10^{12}	60-80 ²
Poly(vinylidene fluoride)	135	2×10^{12}	50-60 ³
Styrene acrylonitrile ¹	80	$>1 \times 10^{14}$	115
Styrene butadiene ¹	65	1×10^{14}	50

1. W. T. Shugg, Handbook of Electrical and Electronic Insulating Materials, IEEE, 1995
2. J. Brandrup and E. H. Immergut, Eds., Polymer Handbook, Wiley-Interscience, New York (1977).
3. Vishn Shah, Handbook of Plastics Testing Technology, Wiley-Interscience, New York (1984).